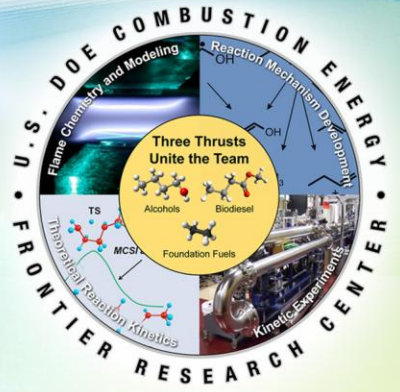


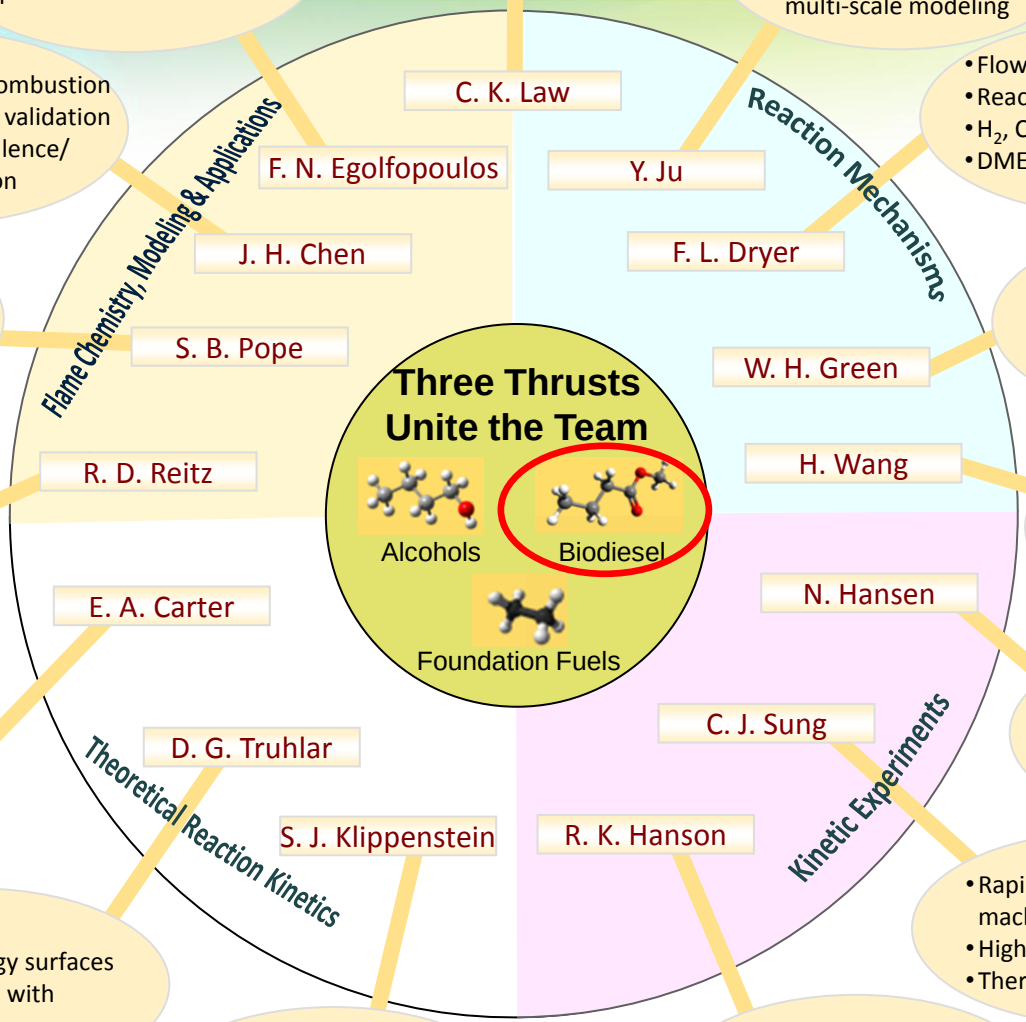
Biodiesel Kinetics and Flame Chemistry

Yiguang Ju, Princeton University

On behalf of CEFRC: Biodiesel Thrust and Flame Chemistry Working Group

Sept. 17-20, 2012, MACCCR

Synergistic 2D Research Structure

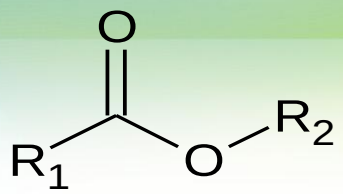


- Laminar flame speeds, extinction and ignition, pollutants
- High-pressure flames
- Turbulent flames
- Droplet processes
- Flame chemistry
- Biodiesel kinetics
- Model reduction & multi-scale modeling
- DNS of HCCI/SACI combustion
- DNS data for model validation
- High pressure turbulence/ chemistry interaction
- Flow reactor experiments
- Reactivity and species history
- H_2, CO, small HC chemistry
- DME, small oxygenates
- LES/PDF/ISAT turbulent combustion
- Turbulence/chemistry
- Mechanisms of butanols
- Automatic mechanism generation
- Low-T combustion engines
- HCCI and RCCI CFD modeling
- Interface with DERC consortium
- Soot
- Small HC chemistry
- Transport properties
- UQ methods
- Ab initio methods
- Thermochemical kinetics
- Ester chemistry
- Flame species by Synchrotron MS
- Burner-stabilized flames
- Potential energy surfaces
- Rate constants with tunneling
- Rapid compression machine
- High-pressure ignition
- Thermometry and species
- Potential energy surfaces
- Reaction rate constants
- High pressure theories
- Shock tube/Laser diagnostics
- Ignition/Species histories
- Rate constants

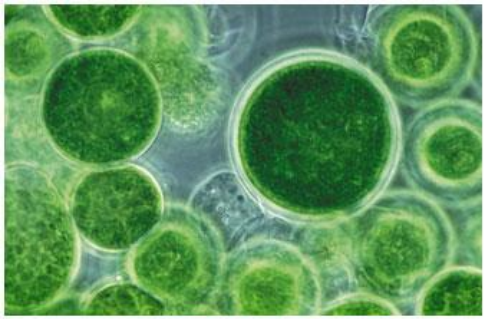
C. K. Law
F. N. Egolfopoulos
Y. Ju
J. H. Chen
F. L. Dryer
S. B. Pope
W. H. Green
R. D. Reitz
H. Wang
E. A. Carter
N. Hansen
D. G. Truhlar
C. J. Sung
S. J. Klippenstein
R. K. Hanson

Motivation

Biodiesel:

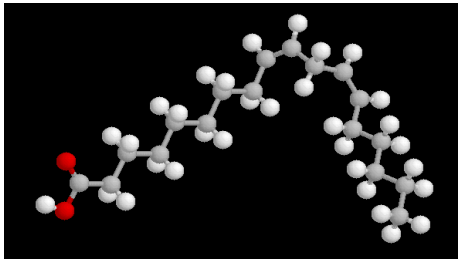


- Produced from vegetable oils, animal fats, & waste materials
- Energy density much higher than ethanol
- 28 billion gallons of biodiesel produced in 2010 worldwide
- Large molecules: C_{16}-C_{18} with ester functional group
- Different combustion chemistry/emissions from hydrocarbons
- Large disparities in alkyl chain length and structures

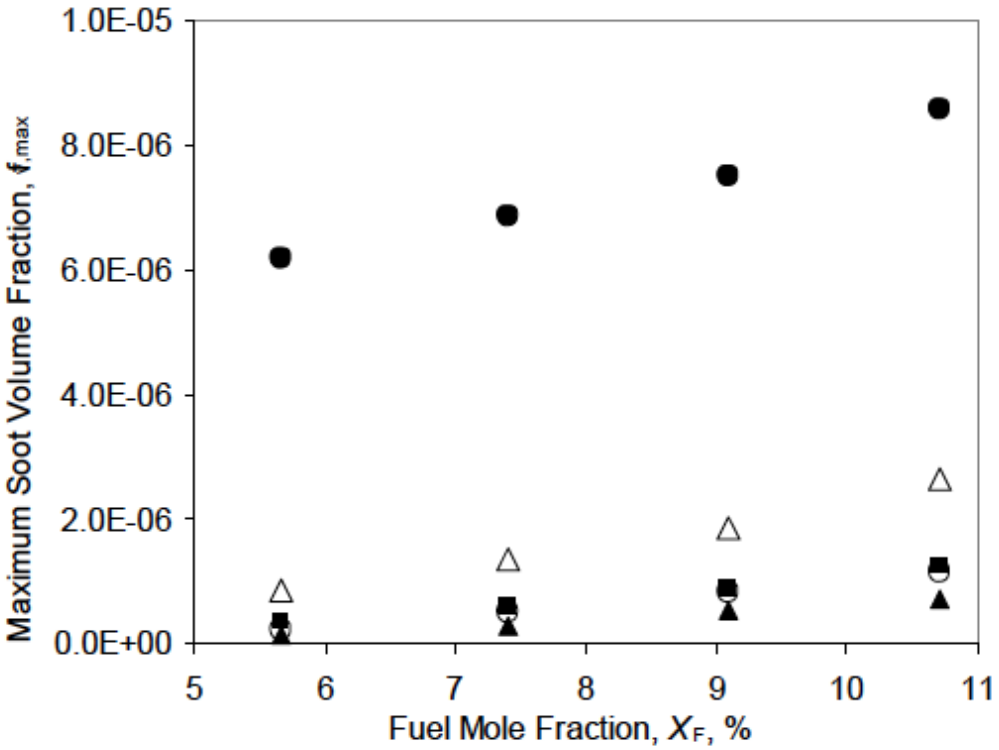


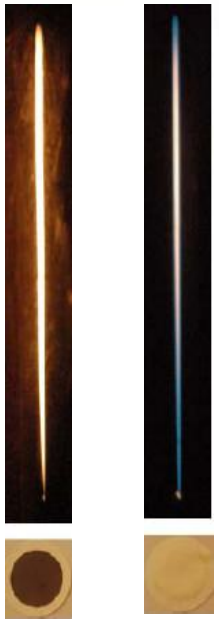
Trans-esterification

Biodiesel



Sooting Propensity of Diesel Surrogate and Large Ester Flames





Diesel Biodiesel
(Law, Princeton)

Maximum soot volume fraction measured in a diesel surrogate, *n*-decane, methyl decanoate, methyl undecanoate, and methyl 10-undecenoate flames; (●) diesel surrogate; (Δ) methyl 10-undecenoate; (■) *n*-$C_{10}H_{22}$; (○) methyl undecanoate; (▲)methyl decanoate.

Diesel surrogate: 70% *n*-$C_{10}H_{22}$ + 30% 1-methyl naphthalene Dagaut and coworkers (2010)

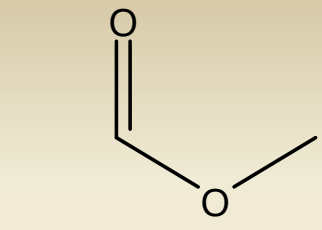
Scientific Questions?

- How to address the knowledge gaps in kinetics of large, oxygenated fuel molecules?
- How can we use quantum chemistry and kinetic experiments to provide a better, predictive model?
- How to address the transport and chemistry interaction in flames?

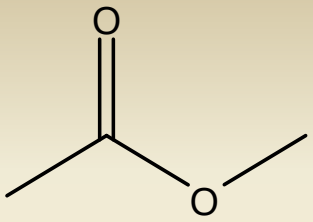
Research Objectives

- Advance the understanding of combustion kinetics of methyl esters
- Develop a validated kinetic methyl ester kinetic mechanism to model oxidation with quantum chemistry calculations
- Advance understanding of chemistry/transport interaction

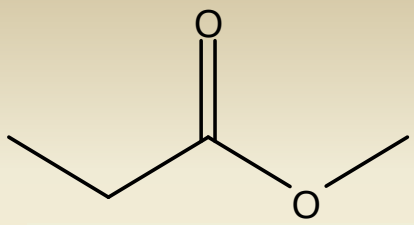
1. Biodiesel Kinetics: Hypothesis



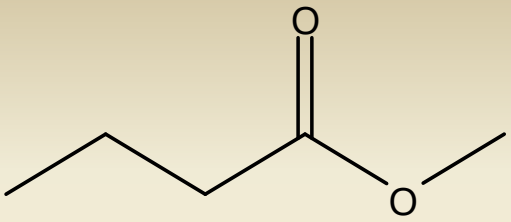
Methyl Formate



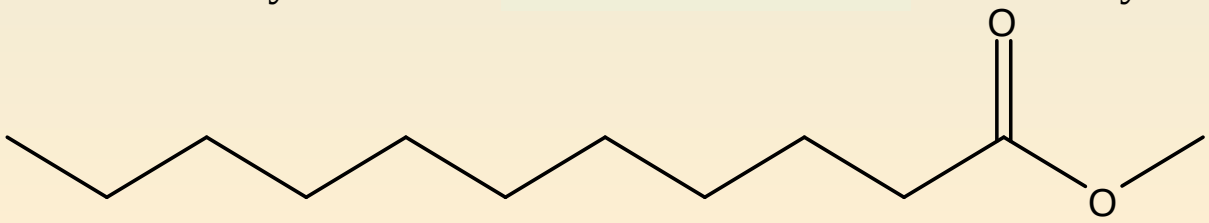
Methyl Acetate



Methyl Propanoate

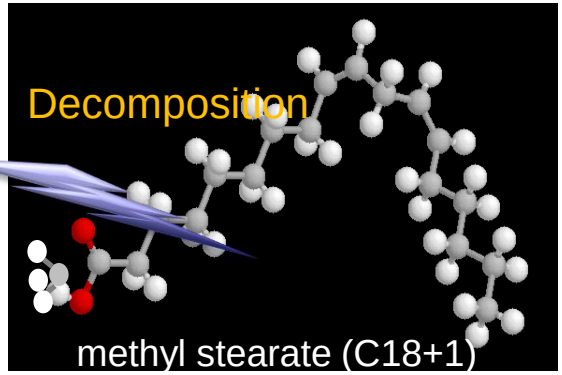


Methyl Butanoate



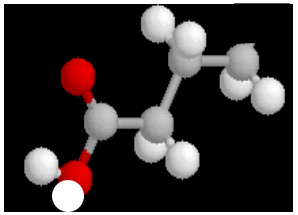
Methyl Decanoate

Similarity between Small/Large Esters?

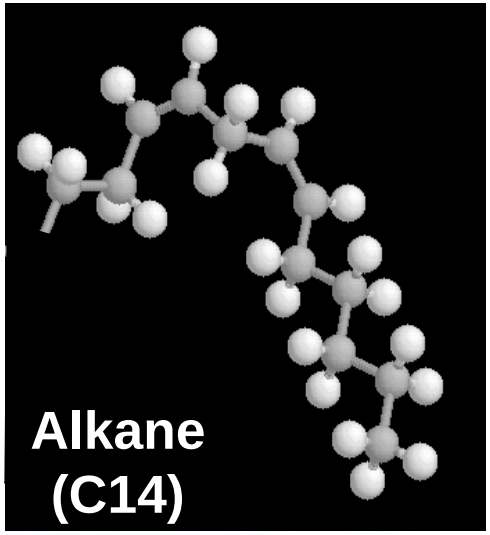


Methyl Butanoate (C4+1)

=

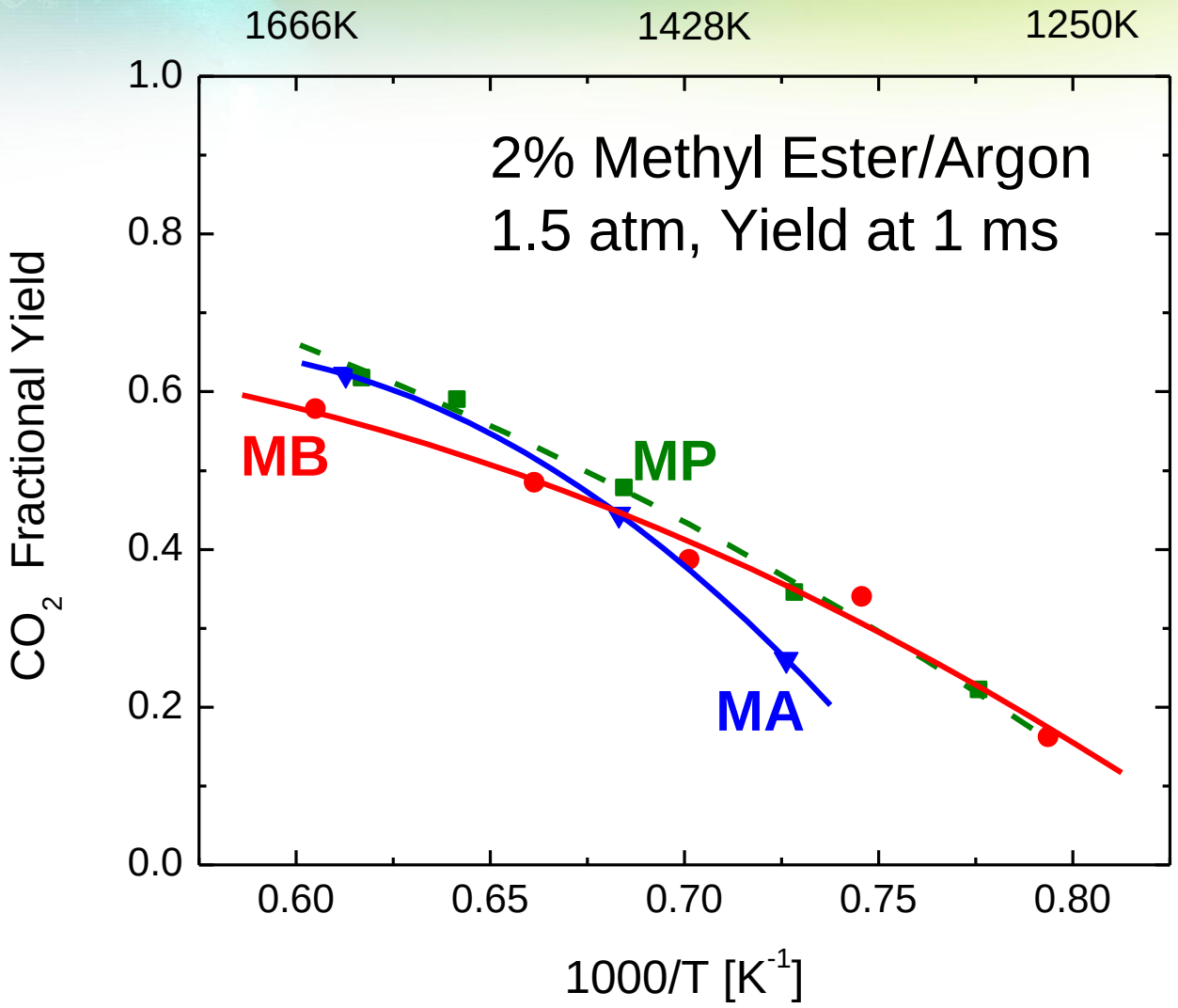


+



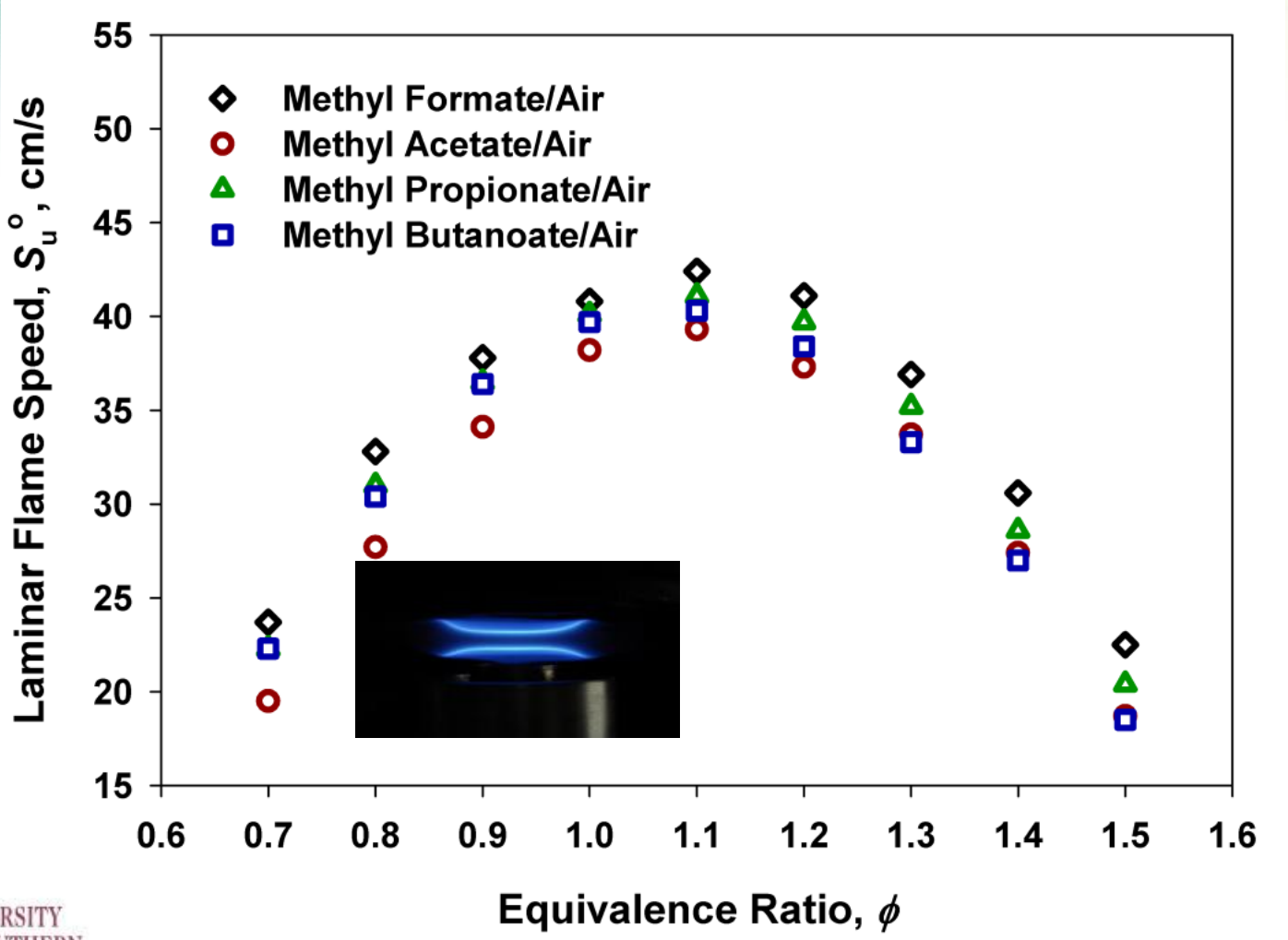
1A. Small Methyl Ester Pyrolysis in Shock Tube

Stanford University



The reactivity is strongly affected by the alkyl chain length

1B. Comparison of Premixed Flame Speeds of Small Methyl-Esters/Air (C_1-C_4: 1 atm)



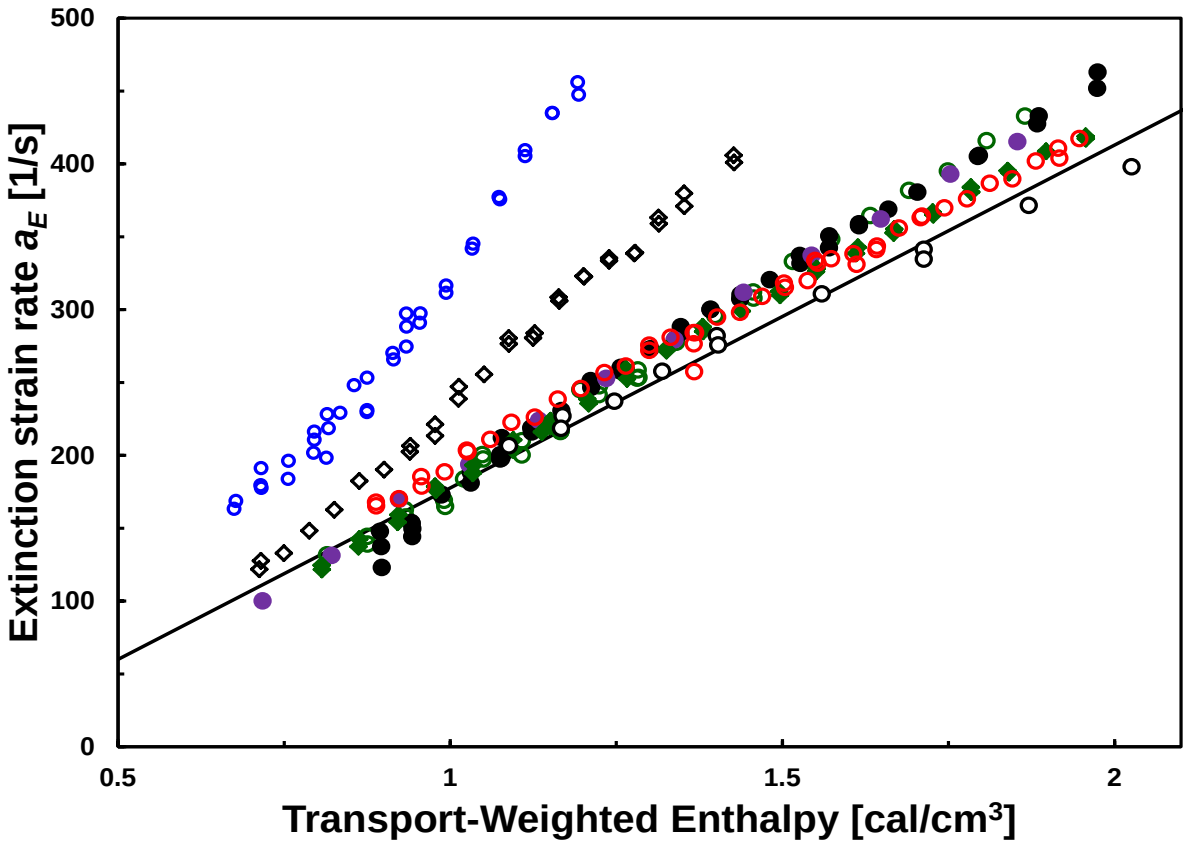
USC UNIVERSITY OF SOUTHERN CALIFORNIA

Egolfopoulos et al.

- Methyl formate has the highest reactivity
- Methyl propanoate is the second

1C. Comparison of Extinction Limits of Methyl Esters (C_1-C_{10})

Extinction limit vs. Transport weighted enthalpy (TWE)



T_f = 500 K, T_{ox} = 298 K

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

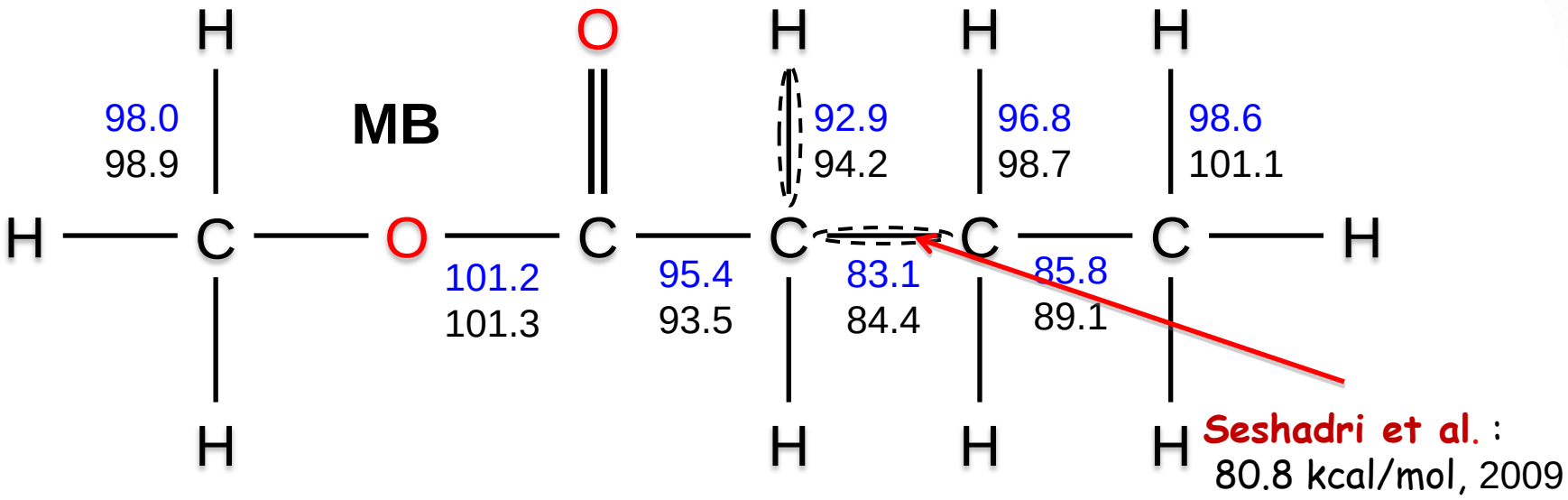
- **Uniqueness of small methyl esters: methyl formate & methyl propanoate**
- **Similarity of large methyl esters**

1D: BDEs (D_{298}) (kcal/mol) in Biodiesel Methyl Butanoate (MB)

MRSDCI /cc-pV∞Z // B3LYP
CBS-QB3-Isodesmic*

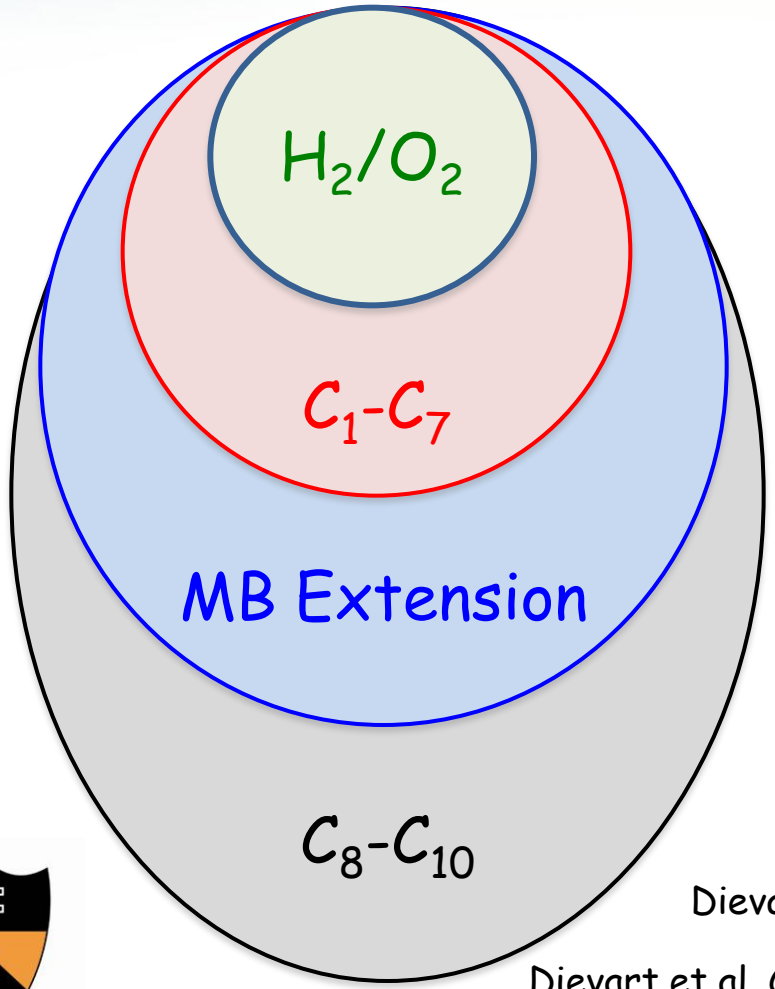
Oyeyemi, V. B.; Pavone, M.; Keith, J. A.; Carter, E. A. *in preparation*, (2012).

* Osmont et al. *J. Phys. Chem. A*, 111, 3727 (2007)



- **Weakest bonds:** dissociated radicals are resonance stabilized.
- **C-C bonds are weaker than C-H bonds:** alkyl fragments allow more structural relaxation than H.

1E. Kinetic Mechanism Development (Ester-MECH: C_2-C_{11} methyl esters)



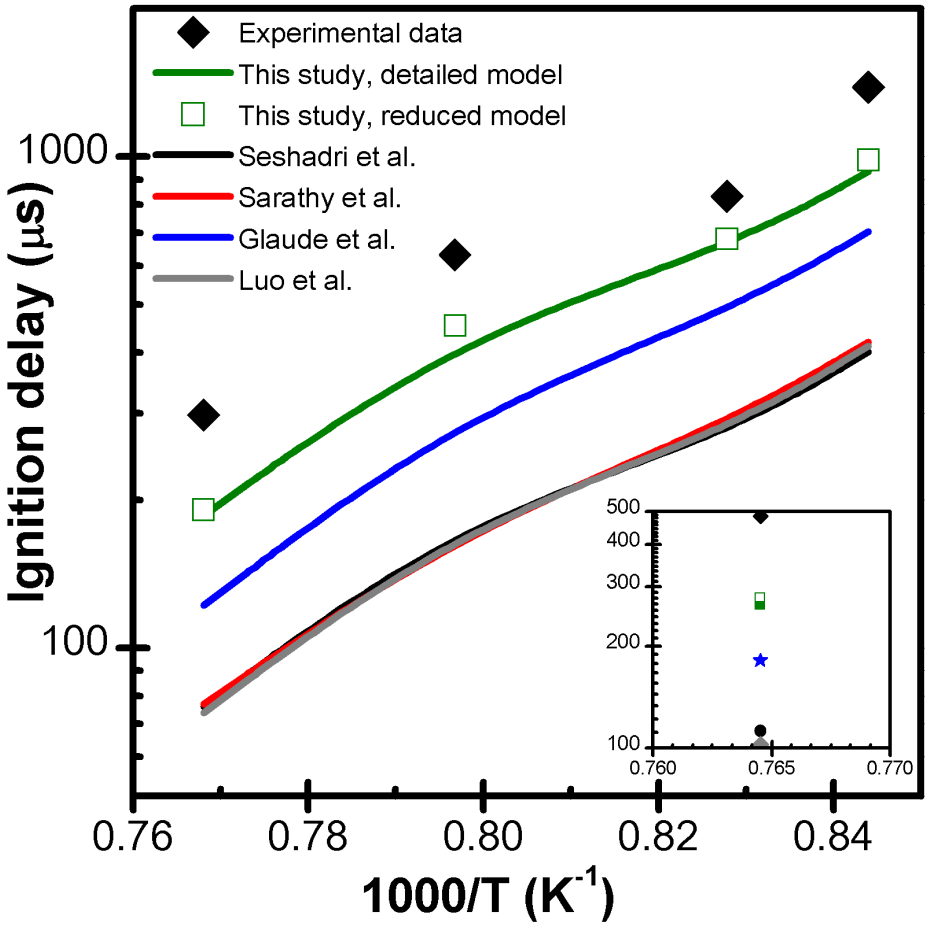
- MB: Ester functional group Dooley et al., 2008
- C1-C7: n-heptane model Curran et al., 2008, 2010
- H_2/O_2: PU hydrogen model

Dievart et al., 34th Symposium on Combustion on Comb., 2012

Dievart et al. Combustion and Flame, 2012, Vol.159 , pp. 1795-1803.

1F. Model Validation: Ignition Delay Time

Ignition delays from Hanson's group (Aerosol Shock Tube, very lean mixtures, diluted in argon, ~7.5 atm)



- ✓ **Present model in good agreement (35%), whereas literature models overestimate MD oxidation rate (50 to 80%)**

Present model, Seshadri et al's model:

Metathesis reactions:	95%
Fuel Decomposition:	5%

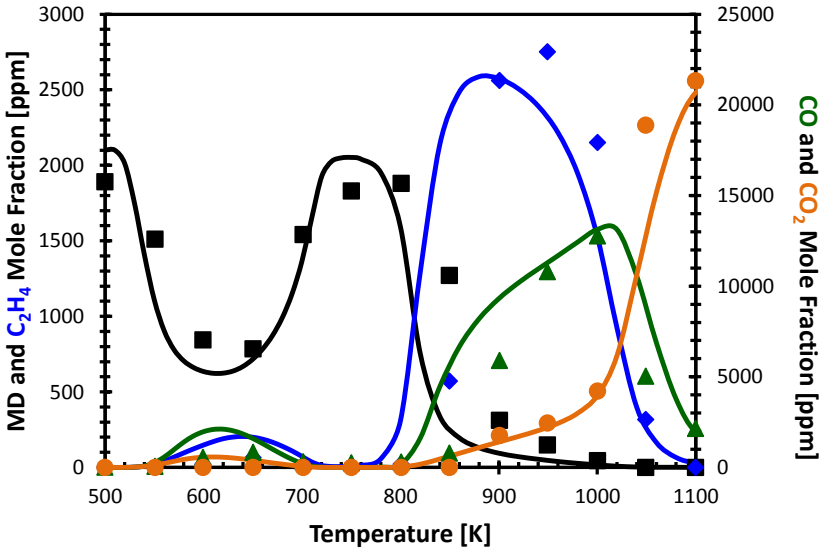
Seshadri et al's model:

Metathesis reactions:	55%
Fuel Decomposition:	45%

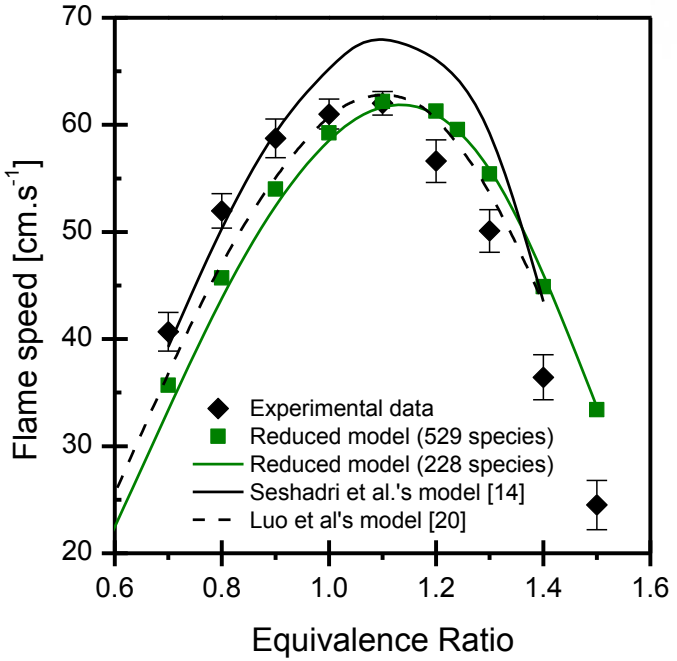
- ✓ **Bond dissociation energy affects strongly fuel decomposition pathway**

Model validation: JSR & Flame speeds

- methyl decanoate
  - high temperature kinetics
  - speciation profiles, flame speeds



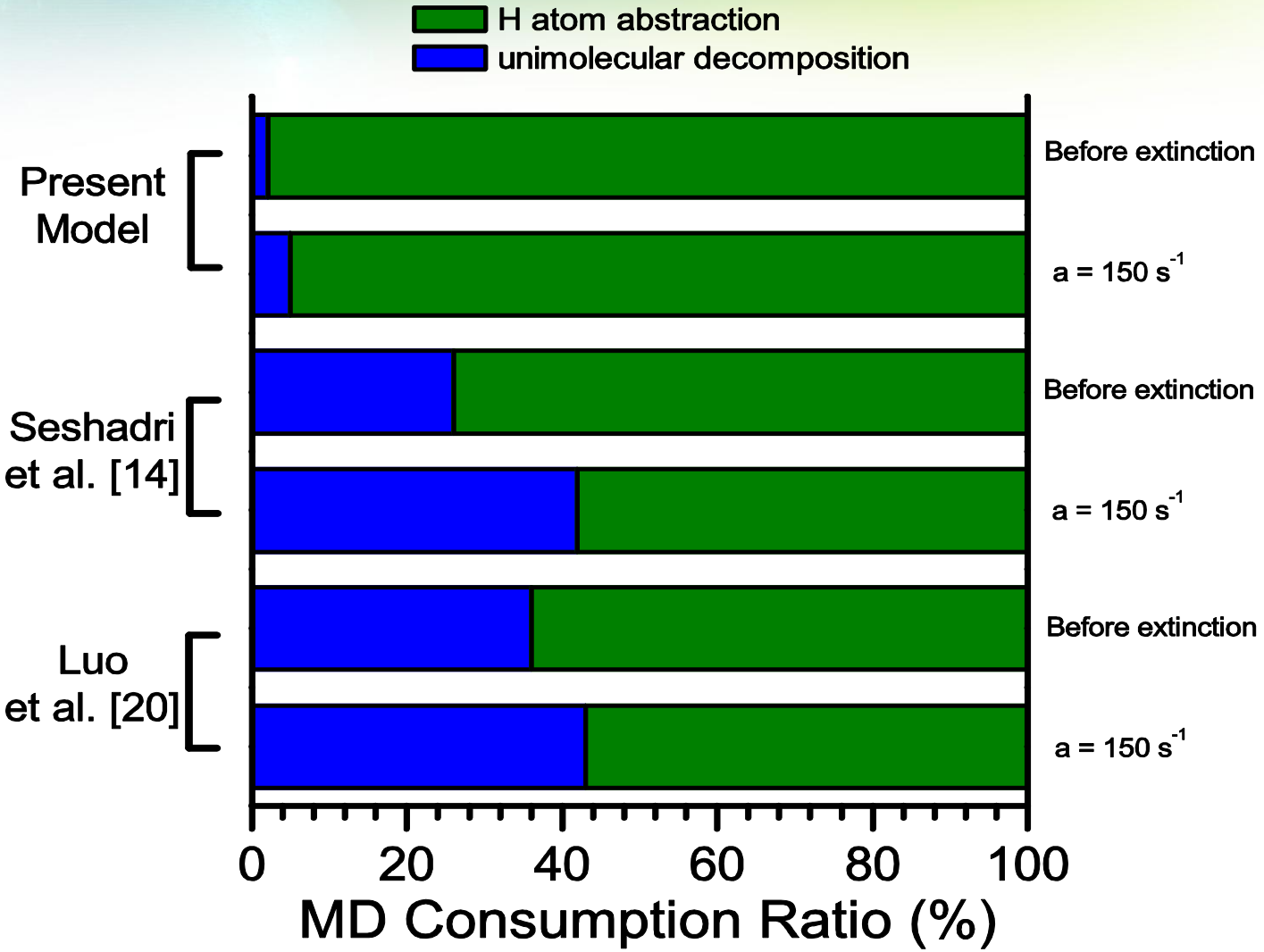
Jet-Stirred reactor (Glaude et al., C&F 157, 2010)
P = 1atm, τ = 1.5 s



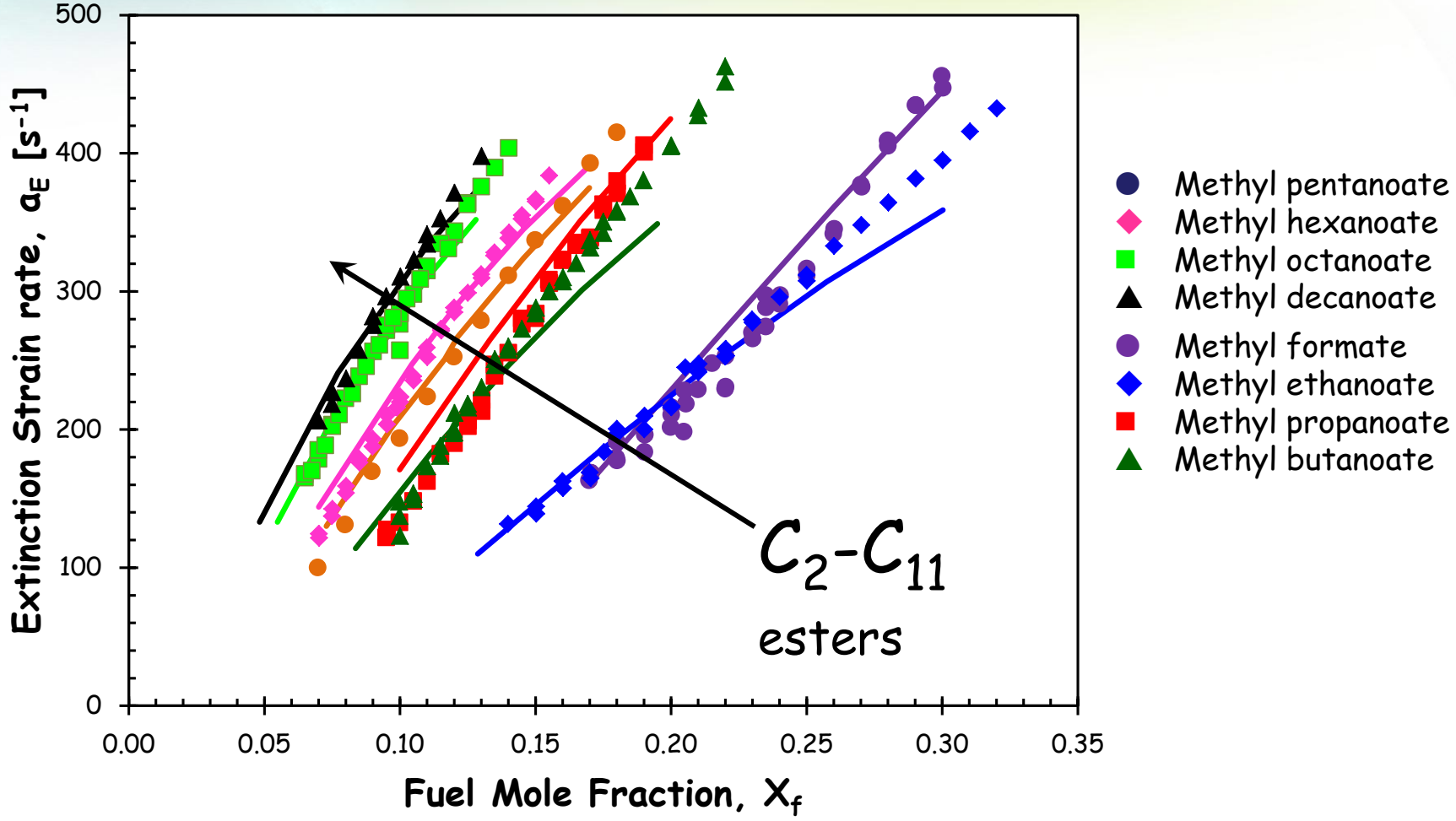
Laminar Flame Speeds
(Wang et al., C&F 158, 2011)
P = 1atm, T = 403 K

R C Glaude et al., CF, 2010.

Model comparison in diffusion flame: MD

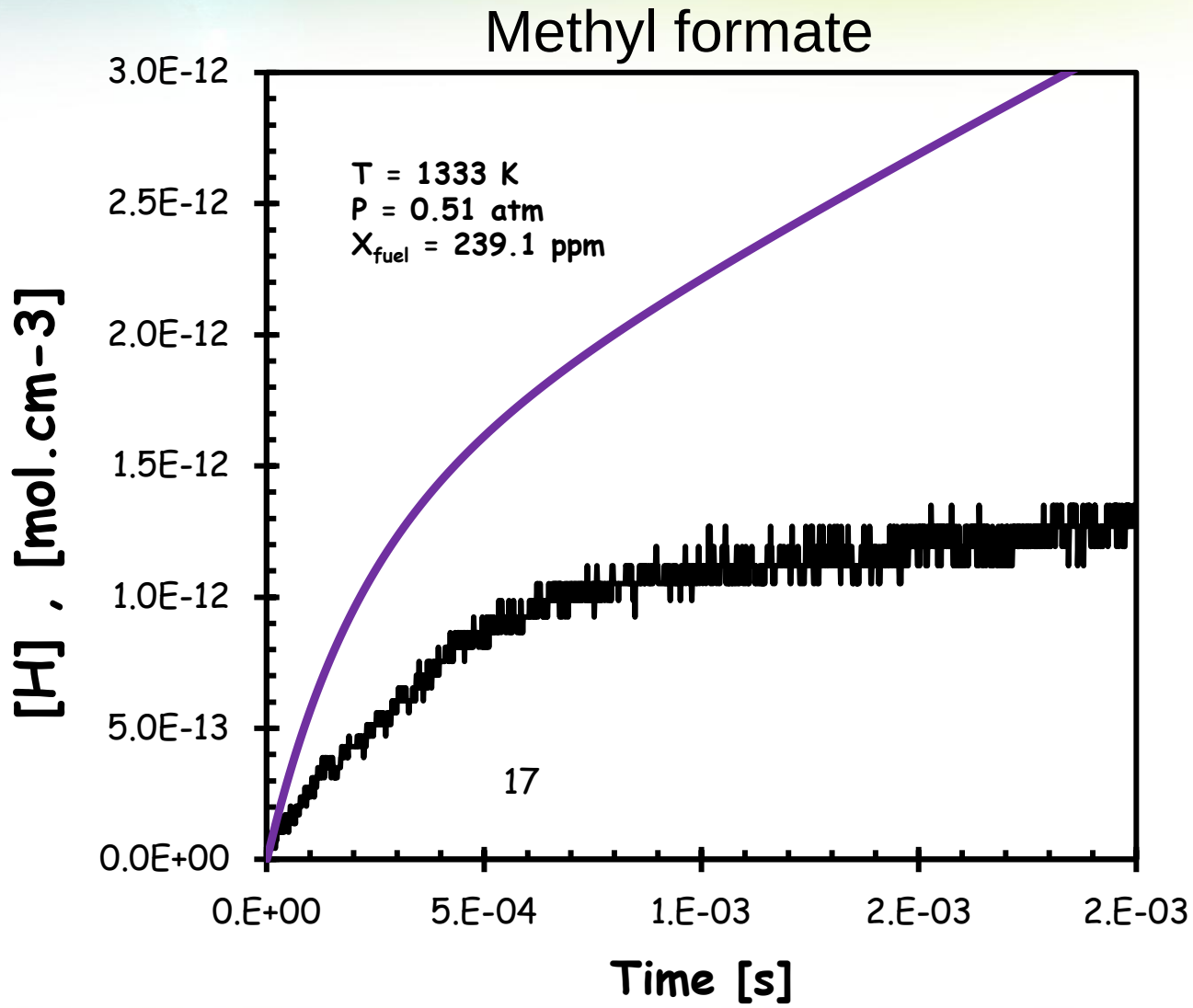


Model validation: Diffusion flame extinction



Dievart et al., 34th symposium on combustion, 2012

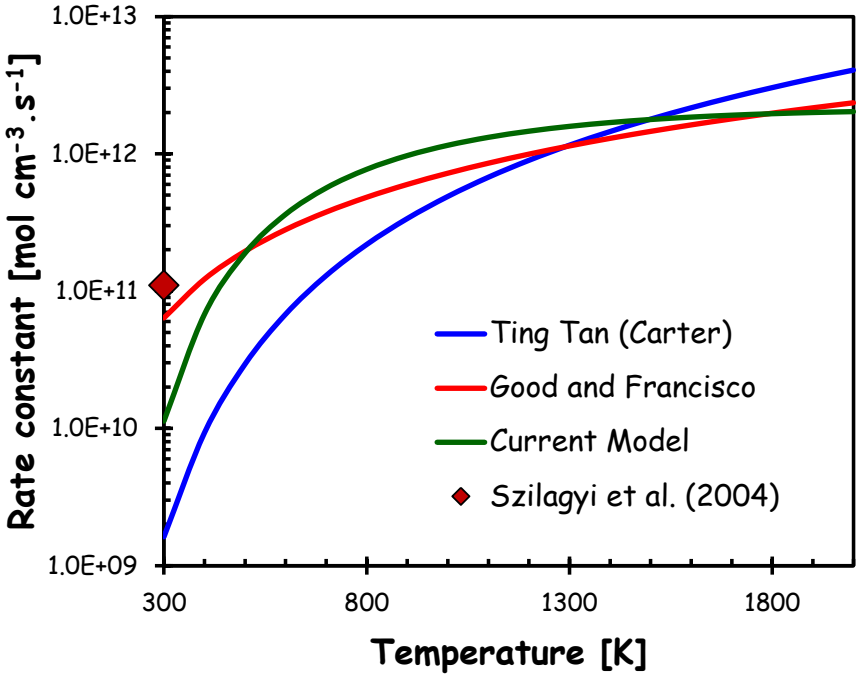
Model validation: Species time history



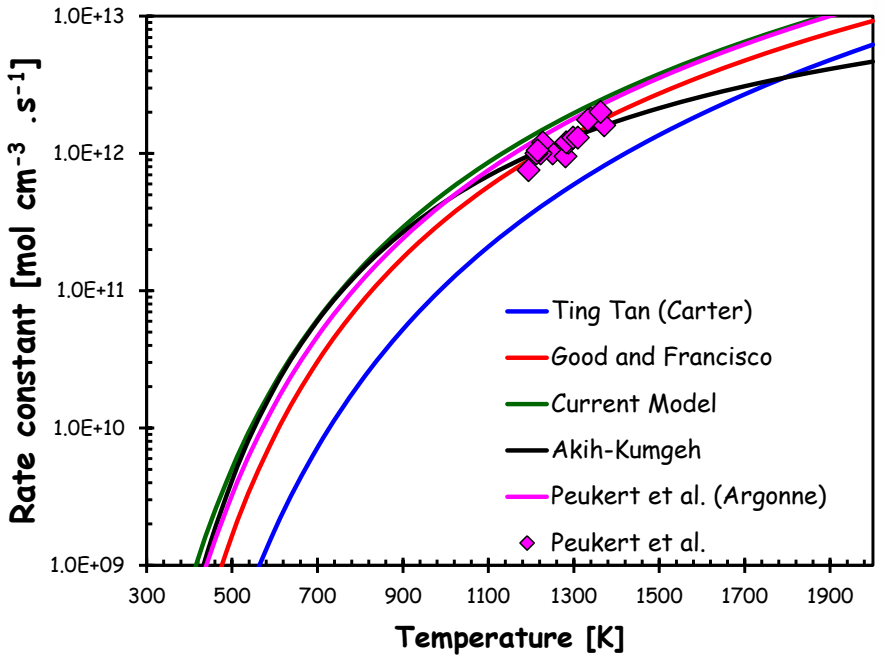
H abstraction reactions by OH and H: Methyl Formate

- Large deviations between the rate constants calculated by the Carter's group (J. Phys. Chem. A, 2012) and the previous estimates or calculations.

$CH_3OCHO + OH = CH_3OCO + H_2O$



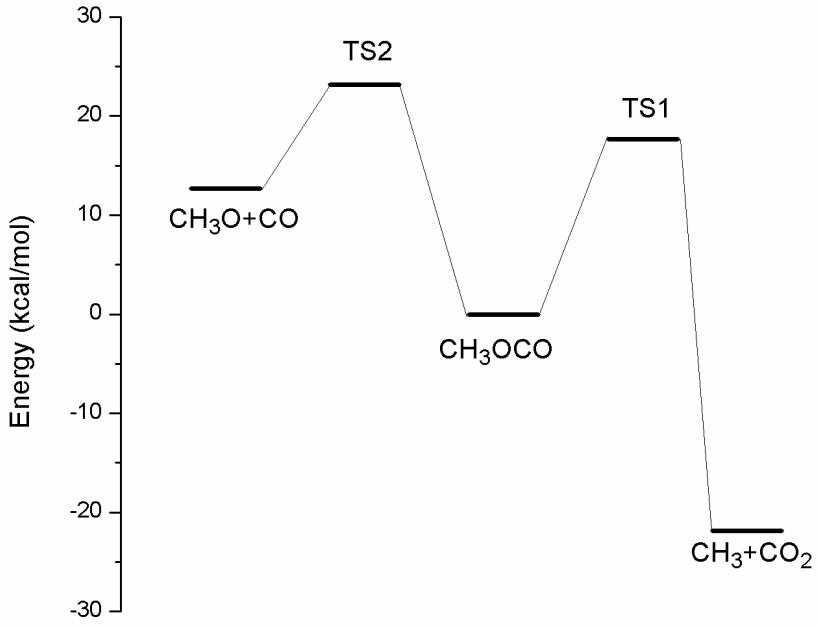
$CH_3OCHO + H = CH_3OCO + H_2$



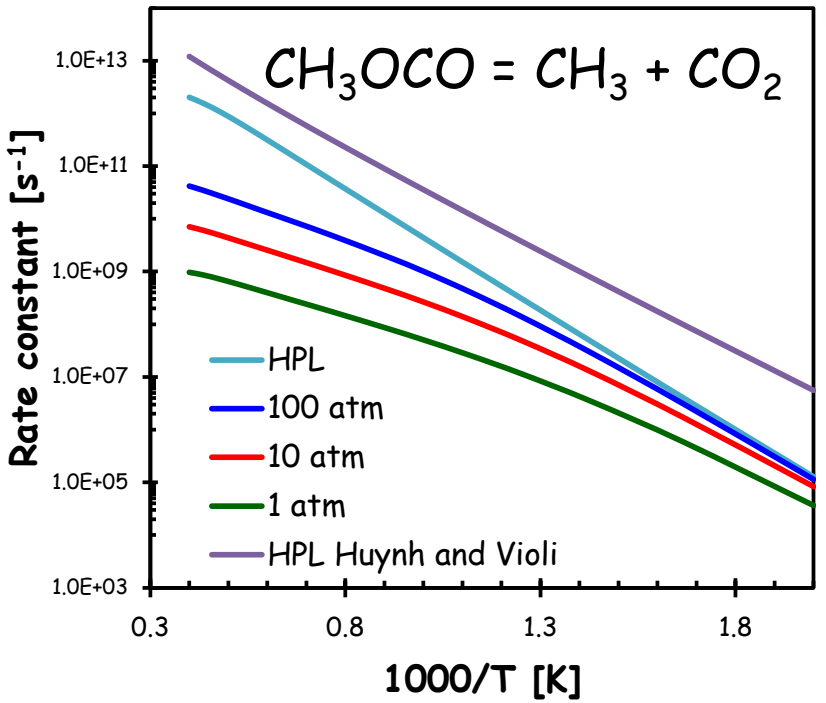
Good and Francisco, J. Phys. Chem. A, 2002, Vol. 106, pp. 1733-1738
Peukert et al., Combustion and Flame, 2012, Vol. 159, pp. 2312-2323
Akih-Kumgeh and Bergthorson, Comb. Flame, 2011, Vol. 158, pp. 1037-1058
Szilagyi et al., J. Phys. Chem, 2004, Vol. 118, pp. 479-492

Methyl-Ester Radical Decomposition Reactions
(Collaborative work : Carter, Klippenstein and Ju)

- Decomposition of small methyl ester radicals such as CH_3OCO (and C_2H_5OCO) are key reactions.
- Literature: only high pressure limit rate constant with low level PES is available (e.g. BH&HLYP/CC-PVTZ).
- Present method: MRACPF/CBS//CASPT2/CC-PVTZ method on PES and VARIFLEX for pressure dependence

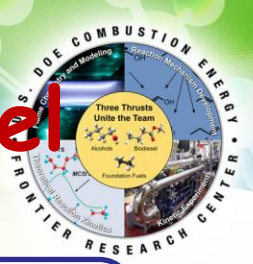


Potential Energy Surface of CH3OCO decomposition at MRACPF/CBS//CASPT2/cc-pvtz



L.K. Huynh, A. Violi. J. Org. Chem. 72 (2008) 94-101.

Collaborative structure of the Biodiesel



Carter

- **Thermochemistry**
  H, Cp, S
- **Rate constants**

MF+X , ME+X, MP+X…
(OH, H, CH_3, HO2)

Yang, Raghu, Ju, Klippenstein

- **Rate constants**
  CH_3OCO
  C_2H_5OCO
  MF, ME, MP…
  Decomposition

Hanson group

- **Rate constants**
  MX+ OH
  X=F,A,P,B
- **Speciation time history**

Ester-MECH
C_2-C_{11} Esters

Dryer, Hansen and Ju

- **Speciation experiments**
  (Flow tube, flames)

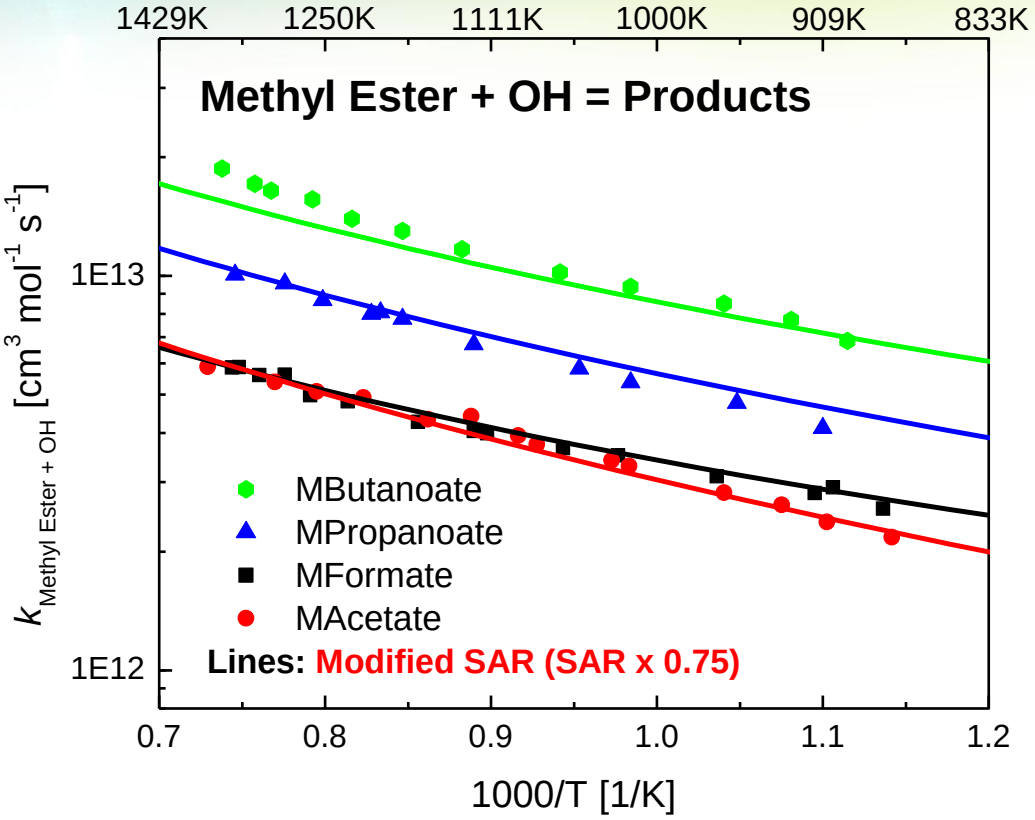
Sung and Hanson

- **Ignition delay**
  (Shock tube, RCM)

Egolfopoulos, Ju, Law

- **Flame speeds**
- **Flame structure**
- **Extinction**
- **Emissions**

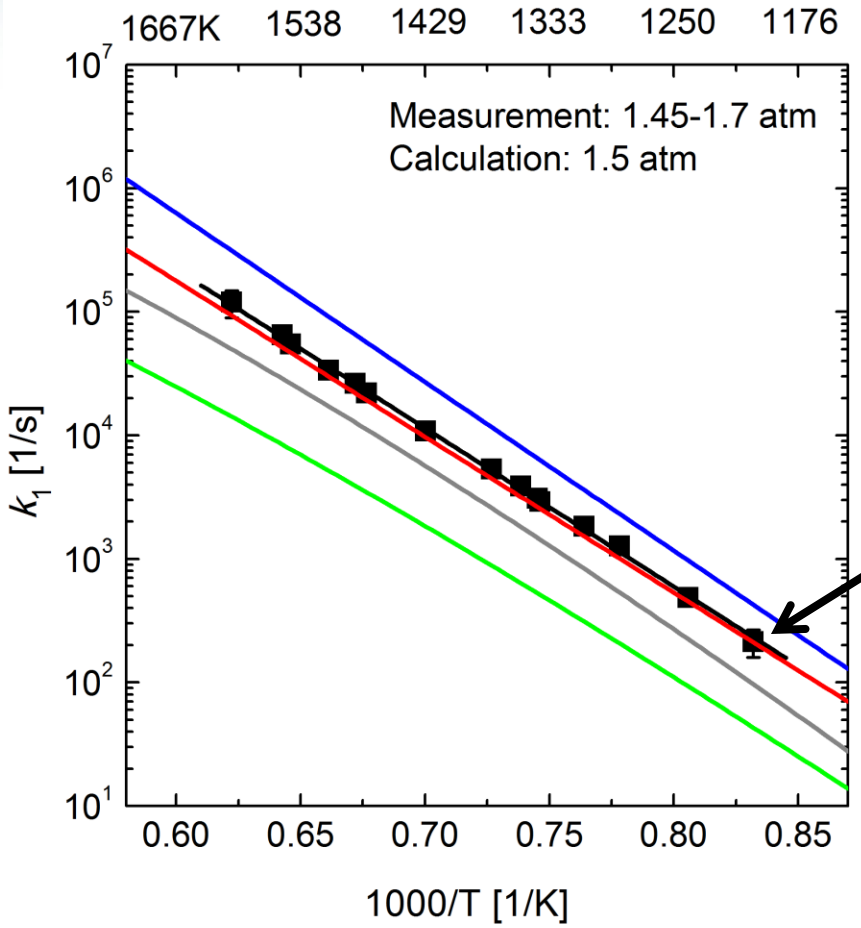
Summary: OH + Methyl Esters → Products



- Data agree within 25% with Structure Activity Relationship (SAR) estimated rate constants (the same rate used in the current model).

Methyl Formate Decomposition Kinetics

Summary Arrhenius Plot k_1: MF → CO + CH_3OH



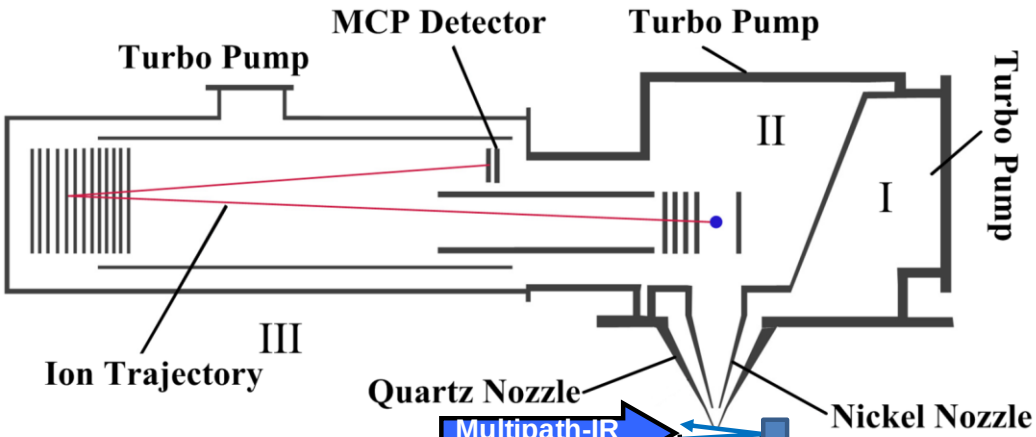
- Wide T range
- Low data scatter
- Repeatable

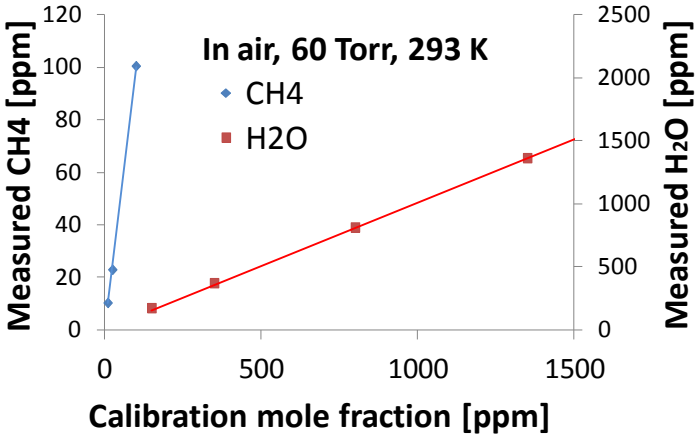
±25%

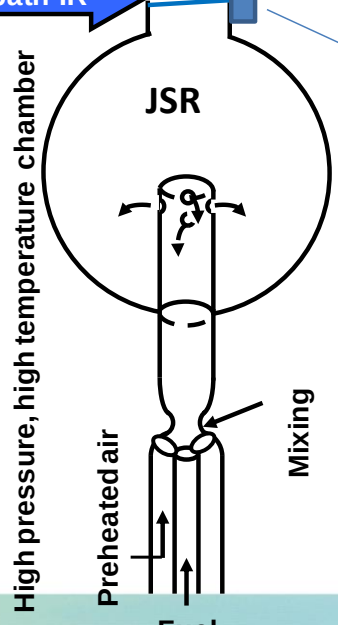
- Experiment, current study
- Westbrook et al. 2009
- Dooley et al. 2010
- Peukert et al. 2012
- Metcalfe et al. 2010

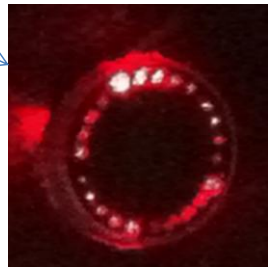
Advanced diagnostics- high pressure reactors at low and intermediate temperatures

MBMS/mid-IR with flow reactor/jet stirred reactor





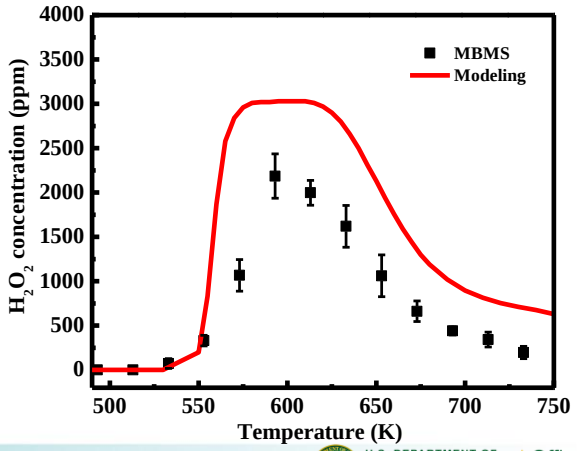




Herriott cell reflections

H_2O_2 Measurements, DME/O_2/He

(2 sec, 1 atm (0.02/0.1/0.88)



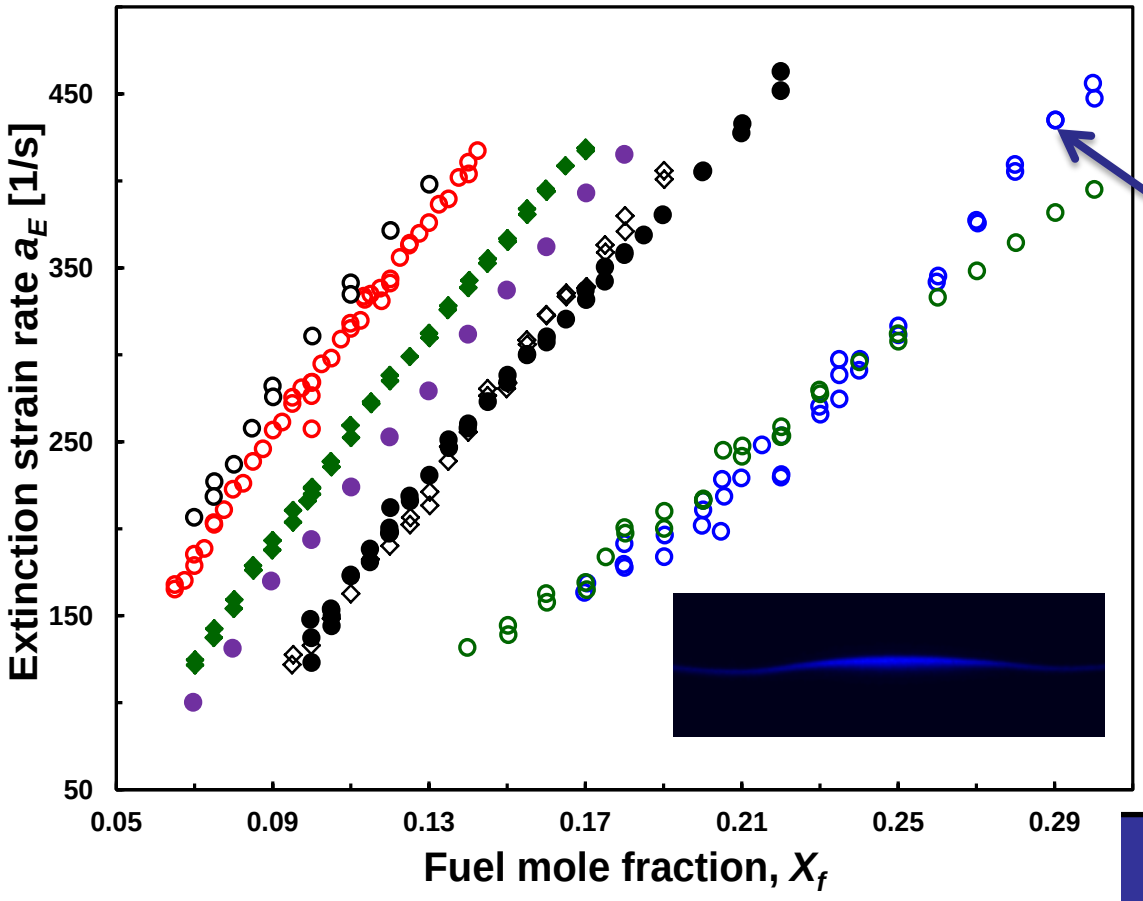
H_2O_2

HO_2 ?

2. Flame Chemistry: Kinetic &Transport Interaction

- **Interaction of Transport and Chemistry on Flame Extinction**
- **Low Temperature Ignition and New Flame Regimes**

2A. Diffusion Flame Extinction Limits: From Methyl Formate to Methyl Decanoate



T_f = 500 K, T_{ox} = 298 K

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

	ΔH_{comb} (kcal/mol)	MW (g/mol)
MB	-651.6	102.14
MD	-1533.3	186.29

How to separate chemistry from transport and fuel heating value?

A generic correlation for extinction limit: Transport weighted Enthalpy & radical index

Theoretical analysis of Extinction Damkohler number

$$\frac{1}{Da_E} = \left[\frac{2}{e} \frac{\tilde{Y}_{O,\infty}}{\tilde{Y}_{F,-\infty}{}^2} Le_F^3 P(\eta_F, Le_F, Le_O) L(\eta_F, Le_F) \right] \left[\frac{1}{\tilde{T}_f - \tilde{T}_{-\infty}} \left(\frac{\tilde{T}_f{}^2}{\tilde{T}_a} \right)^3 \exp\left(-\frac{\tilde{T}_a}{\tilde{T}_f} \right) \right]$$

Extinction Strain Rate

$$a_e \propto \frac{1}{\sqrt{M_F / \overline{M}}} \frac{Y_{F,-\infty} Q_F}{C_p (T_f - T_{-\infty})} * R_i$$

Transport

Heat release/heat loss

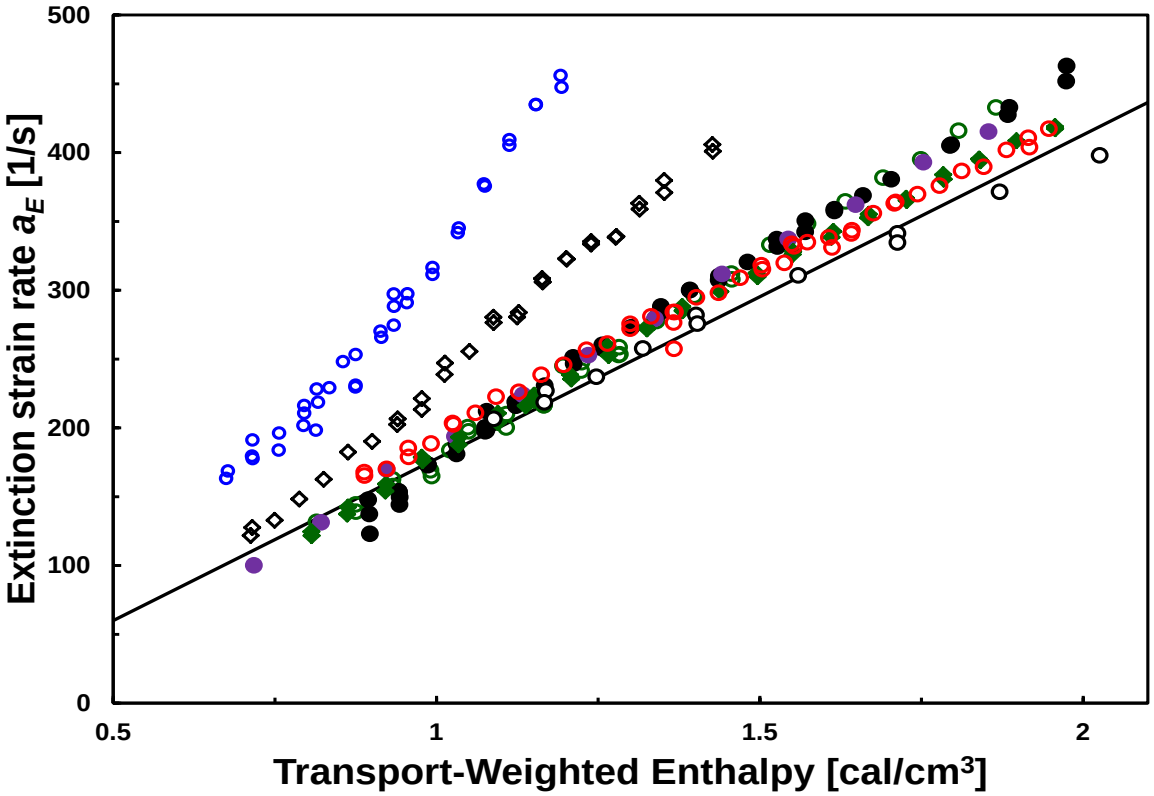
Fuel chemistry
Radical production rate

Transport weighted Enthalpy *Radical index

Won et al. CNF 159 (2012)

Reactivity Scaling of Small/Large Methyl Esters: From Methyl Formate (C_1) to Methyl Decanoate (C_{10})

Extinction limit vs. Transport weighted enthalpy (TWE) flux



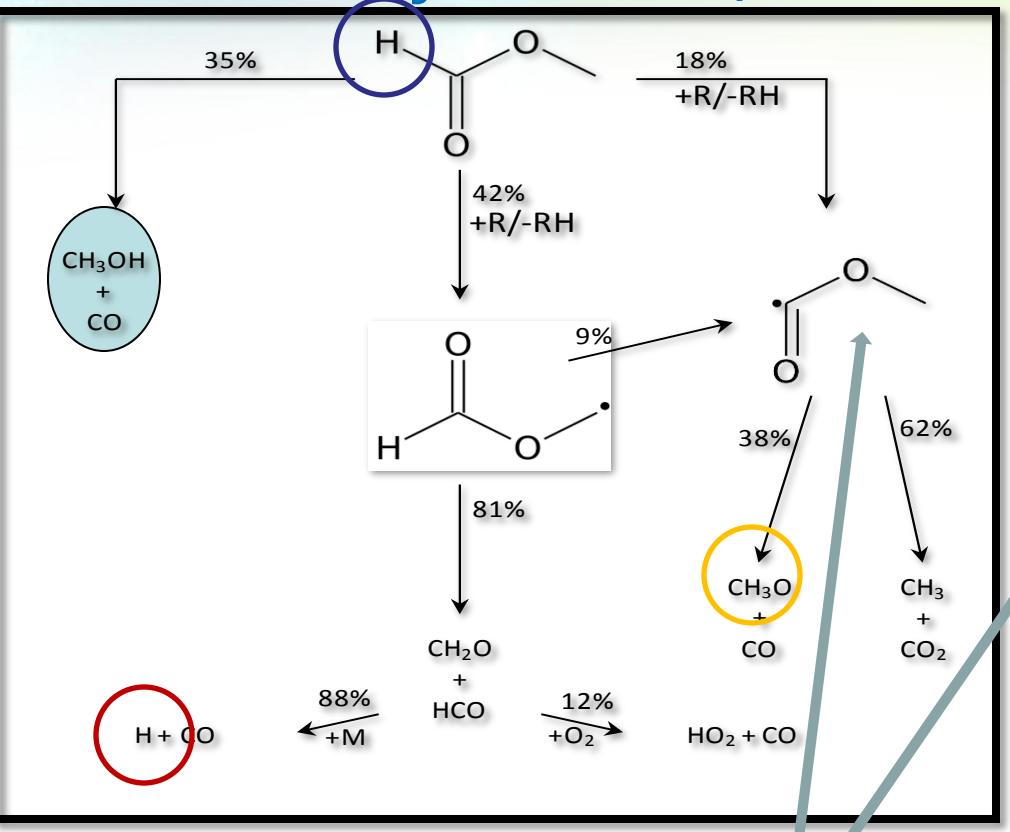
T_f = 500 K, T_{ox} = 298 K,

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

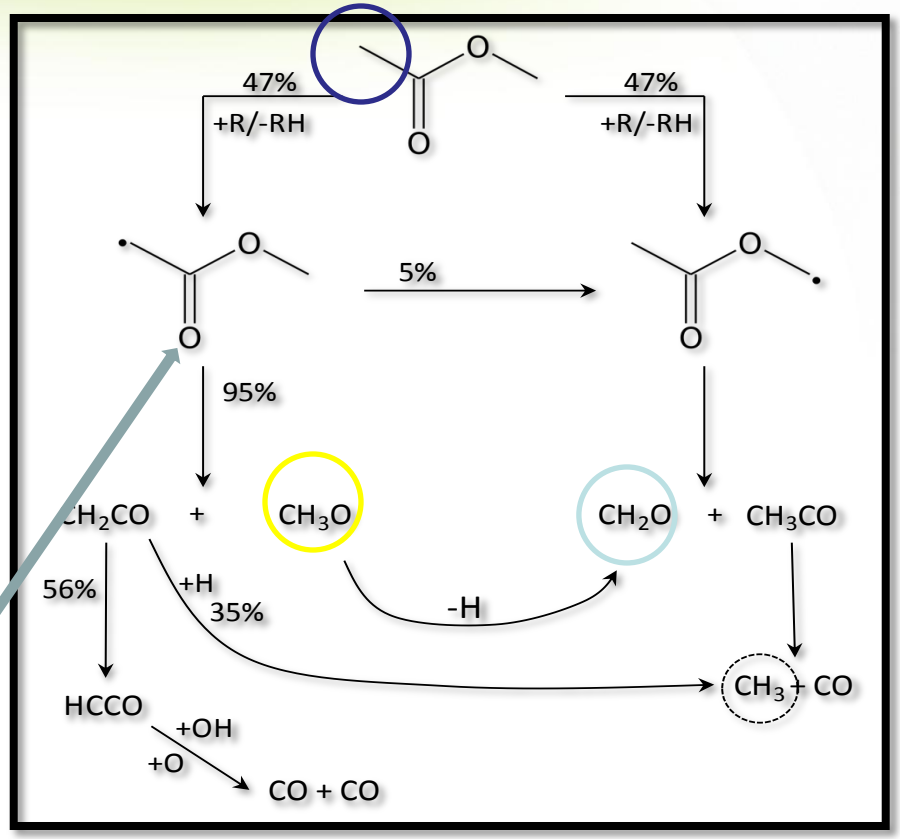
- Uniqueness of small methyl ester
- Similarity of large methyl ester

Impact of alkyl chain length on methyl ester reactivity

Methyl Formate, R0C



Methyl Acetate, R1C



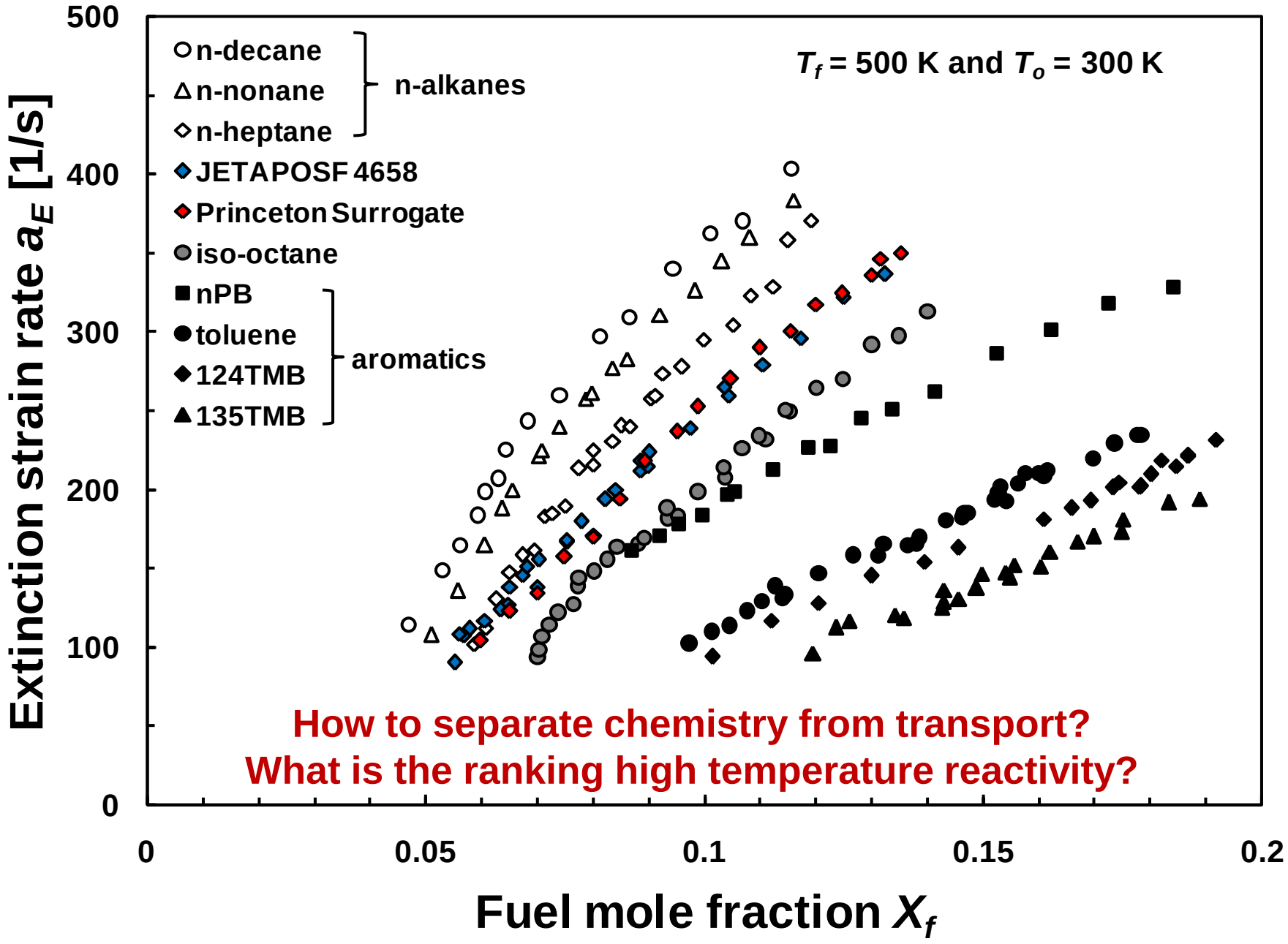
Higher reactivity

Lower reactivity

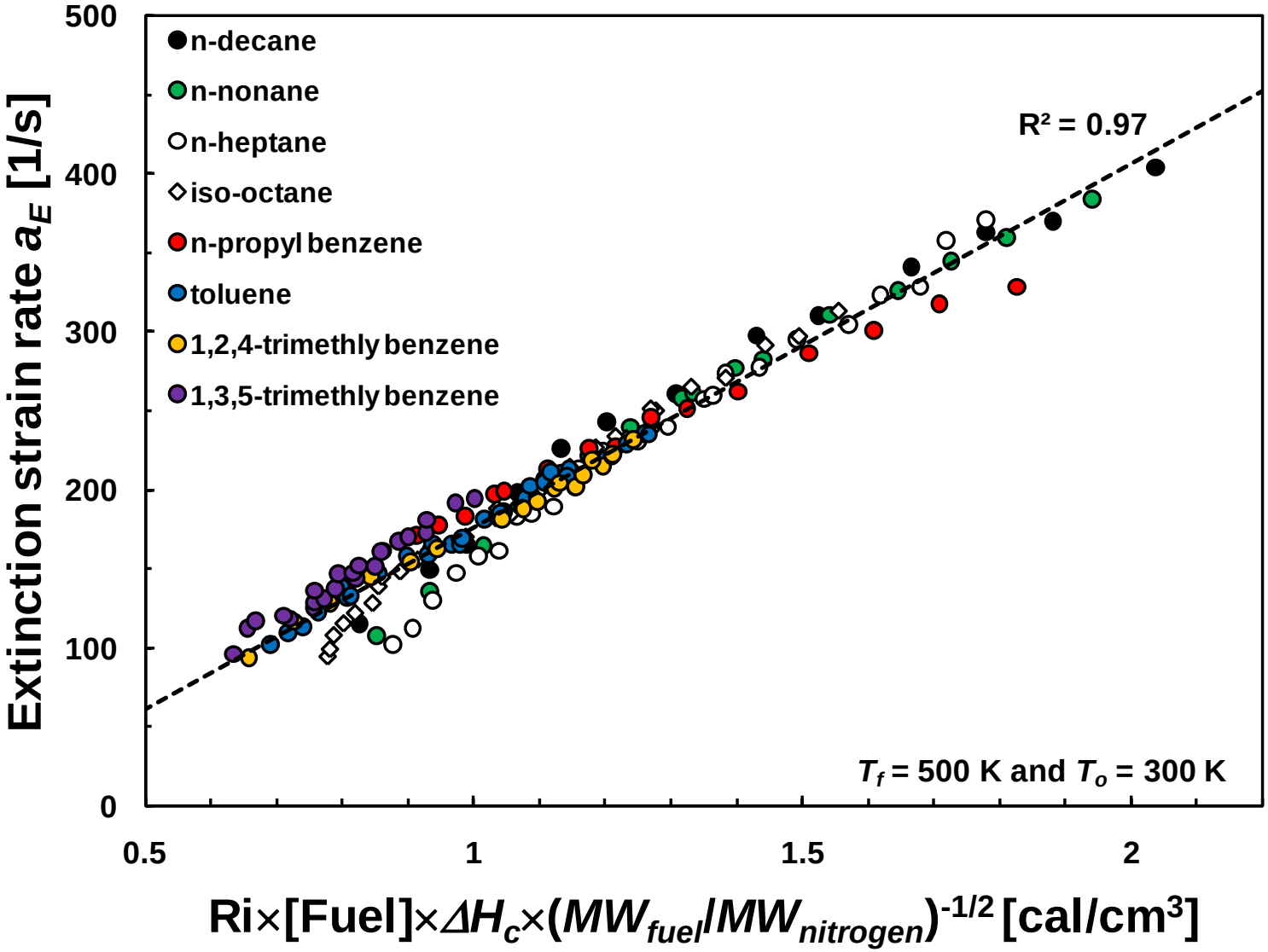
H abstraction reactions, Fuel, CH3OCO, and CH3OC(O)CH2 decomposition reaction rates

Diévart et al, 2012
to presented on Monday at 34th Symposium

Extinction Limit: n-Alkanes, iso-Alkanes, Aromatics

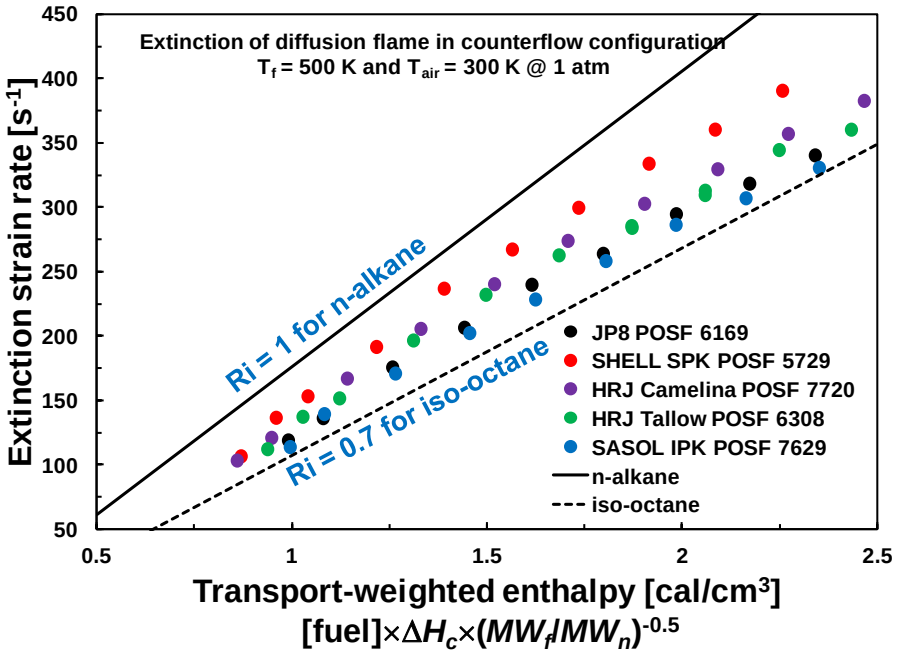


A General Correlation of Hydrocarbon Fuel Extinction vs. TWE and Radical Index



Radical Index for Screening of Alternative Fuels

- Extinction limits of diffusion flames for pure fuel samples have been completely measured and compared by using **TWE**
  - **Heat of combustion, ΔH_c** has been re-estimated based on H/C ratio correlation.
  - Re-evaluation of ΔH_c might be necessary.
- High temperature reactivity based on Radical index
  - SPK ≥ HRJ camelina ≥ HRJ Tallow > JP8 ≥ IPK (~iso-octane)
  - Similar order to DCN measurements, IPK must be heavily isomerized.



Fuel	Radical Index	DCN
JP8 POSF 6169	0.78	47.3
SHELL SPK POSF 5729	0.85	58.4
HRJ Camelina POSF 7720	0.82	58.9
HRJ Tallow POSF 6308	0.8	58.1
SASOL IPK POSF 7629	0.76	31.3

Won et al. CNF 159 (2012)

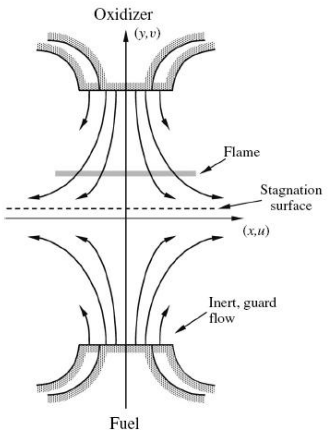
2B. Effects of Transport on Low Temperature Ignition in Non-premixed Counterflow Flames

Law's group

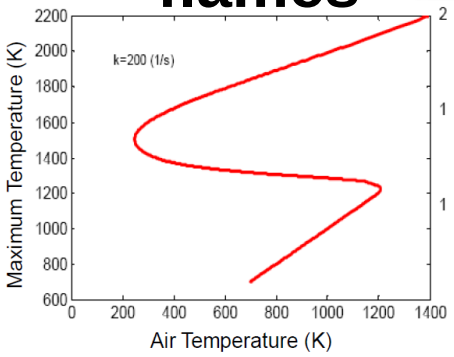
- **NTC behavior extensively observed for homogeneous systems**
- **Corresponding non-monotonic behavior signaling NTC chemistry in steady state strained has not been well studied in flows (e.g. counterflow),**

  Seshadri et al., CF 2009.
- **Reason: Reduced residence time => higher ignition temperature => shifting away from NTC temperature regime**
- **Explore possible existence of NTC behavior for flows**
  - **with low strain rates**
  - **at high pressures**

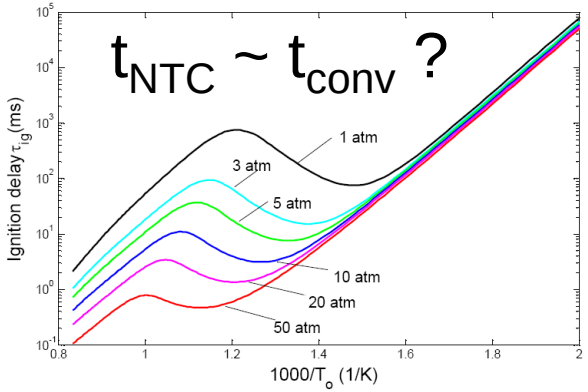
$t_{NTC} > t_{conv}$



Heptane/air flames

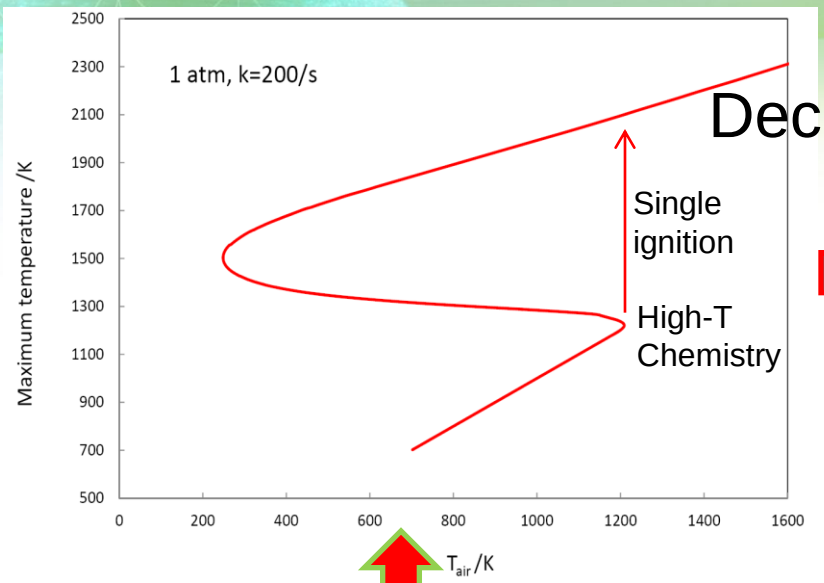


No NTC at 1 atm, 200/s

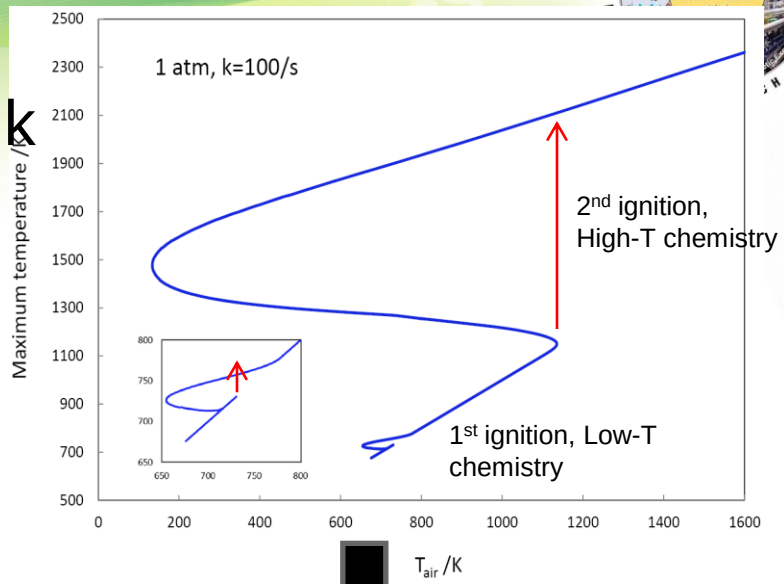


NTC temp. ↑ as pressure ↑

n-Heptane vs. Air in Counterflow Ignition

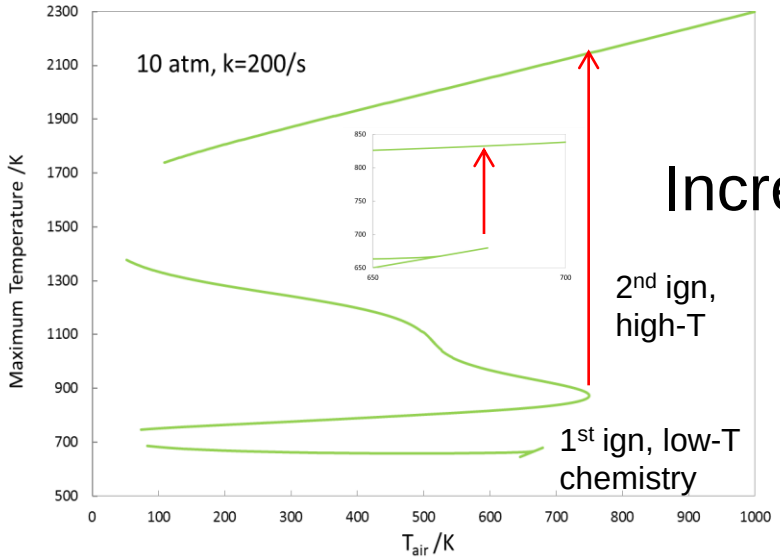


Decrease k

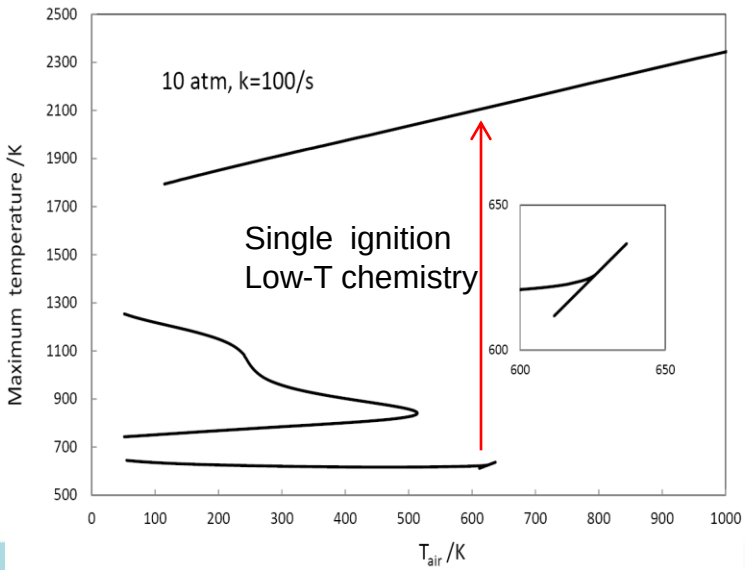


Decrease P

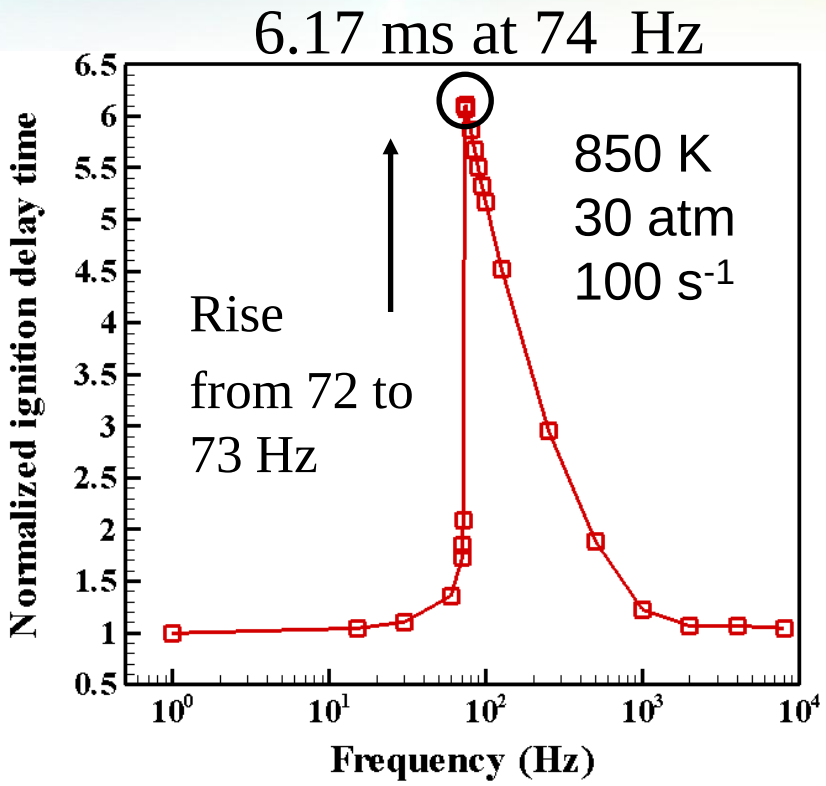
Increase P

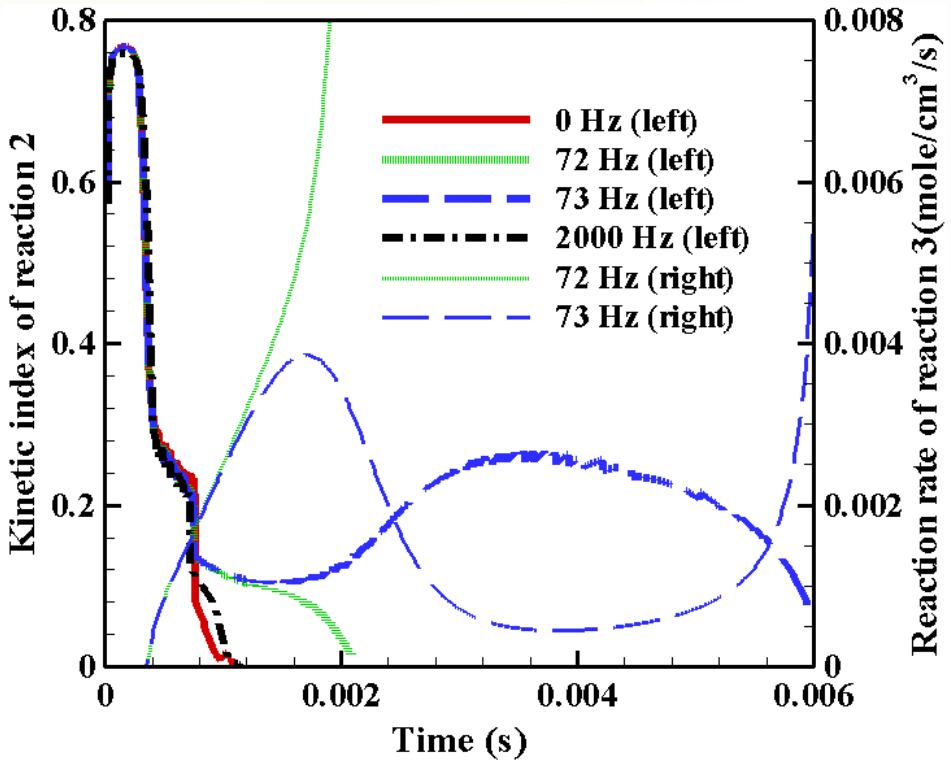


Increase k



Unsteady Flow Perturbation on Low Temperature Ignition in Diffusion Flame





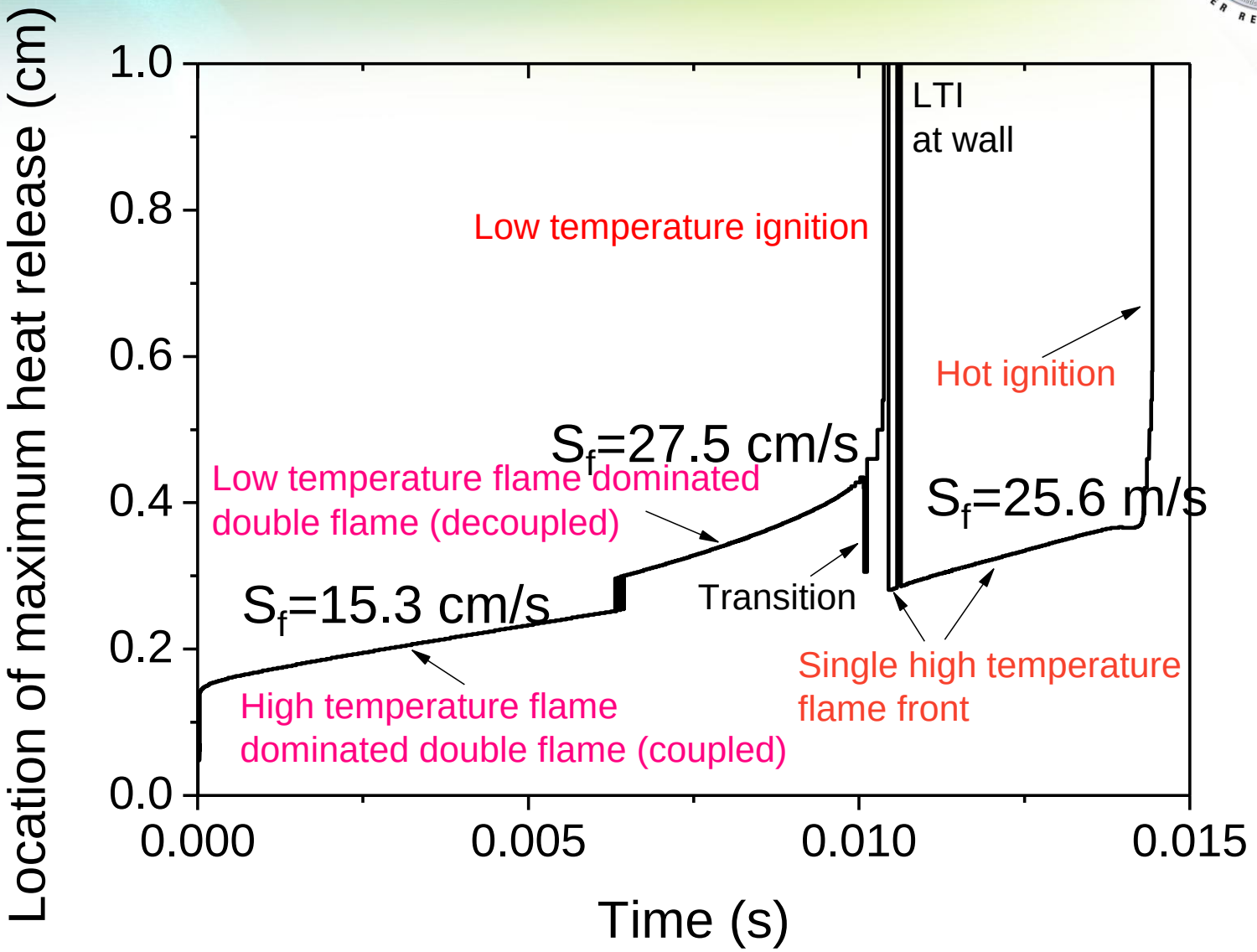
Reaction 2: $RO_2 = R'O_2H$

Reaction 3: $H_2O_2 + M = 2OH + M$

- No effect on initial RO_2 formation,
- H_2O_2 decomposition is delayed by heat loss at high strain rate.

Multi Flame Regimes in HCCI Ignition n-Heptane: Flame Initiation by a Spark at 40 atm, T=700 K

Movie



Conclusions

- Combustion properties, species, and kinetic data methyl esters are experimentally measured by a collective effort.
- An updated methyl ester (C_2-C_{11}) kinetic mechanism is developed and partially validated.
- Large uncertainties in elementary rate constant and species time history.
- Flame theory to correlate flame extinction with TWE and radical index. Uniqueness and similarity of high temperature reactivity of methyl esters are demonstrated.
- Significant impacts of low temperature ignition on ignition and flame propagation are demonstrated. New flame regimes are identified.

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